Final Report

Impact Evaluation of Stream Flow Augmentation with Tertiary Treated Recycled Water

Megan H. Plumlee and Martin Reinhard
Department of Civil and Environmental Engineering
Stanford University
Stanford, CA 94305

Prepared for:

Santa Clara Valley Water District

The Metropolitan Water District of Southern California
Agreement No. 41808

California Department of Water Resources
“Safe Drinking Water, Clean Water, Watershed Protection and
Flood Protection Act”

November 2008

Project Managers

Pam John, Jeannine Larabee, Henry Barrientos (Santa Clara Valley Water District)

Co-sponsors

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118

WateReuse Foundation
635 Slaters Lane, 3rd Floor
Alexandria, VA 22314

Legal Notice

This report was prepared as a result of work sponsored by the California Department of Water Resources, the Santa Clara Valley Water District and the WateReuse Foundation. Content and opinions expressed in this report do not necessarily represent the views of these agencies, their employees, or the State of California.

These agencies, the State of California, its employees, contractors, and subcontractors make no warranty, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the use of this information will not infringe upon privately owned rights.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the contributions of the post-doctoral researchers, undergraduates, Master’s students, visiting scholars and professors who contributed their expertise and enthusiasm to this project over the years, as well as authored and co-authored research included in this report. These people include Chris Gurr, Montserrat Lopez Mesas, Ph.D., Elisabeth Janssen, Eduard Hoehn, Ph.D., Andy Heidlberger, Eva Steinle-Darling, Ph.D., John Montgomery-Brown, Ph.D., Yongmei Li, Ph.D., and Bin Xu, Ph.D. Yongmei Li and Bin Xu (both from Tongji University, Schanghai, China) and Eduard Hoehn (ETH, Zuerich, Switzerland) were supported by their home institutions while working on this project. Megan Plumlee was supported by a National Science Foundation Graduate Research Fellowship.

TABLE OF CONTENTS

EXECUTIVE SUMMARY 1

Abstract 4

1.0 INTRODUCTION 5

- 1.1 Overview 5
- 1.2 Background 5
- 1.3 Project Rationale 6
- 1.4 Project Objectives 7

2.0 PROJECT APPROACH 8

- 2.1 Site selection and hydrology 8
  - 2.1.1 Surface water sampling sites and hydrology 8
  - 2.1.2 Installation of groundwater wells 11
  - 2.1.3 Hyporheic zone 12
- 2.2 Characterization of water quality 12
  - 2.2.1 Selection of target analytes 12
  - 2.2.2 Analytical methods 15
- 2.3 Laboratory investigations of contaminant fate 18

3.0 PROJECT OUTCOMES 19

- 3.1 Characterization of water quality 19
  - 3.1.1 Pharmaceuticals, hormones, organophosphates, plasticizers and oxadiazon 19
  - 3.1.2 Alkylphenol ethoxylate metabolites (APEMs) 23
  - 3.1.3 N-Nitrosodimethylamine (NDMA) 24
  - 3.1.4 Perfluorochemicals (PFCs) 25
  - 3.1.5 Summary of 2005 baseline water quality study 30
- 3.2 Assessment of PFC Occurrence and Toxicity in Wastewater and the Aquatic Environment 32
- 3.3 Characterization of site hydrology and hydrogeology 32
- 3.4 Laboratory investigations of contaminant fate 33
  - 3.4.1 Biodegradation of NDMA 33
  - 3.4.2 Direct photolysis of NDMA 34
  - 3.4.3 Biodegradation of APEMs 36
  - 3.4.4 Indirect photolysis of PFCs 37
- 3.5 PFC removal by membranes in advanced wastewater treatment 38

4.0 CONCLUSIONS AND RECOMMENDATIONS 39

5.0 REFERENCES 42

LIST OF TABLES

Table 1. Description of sites from Figure 3, the final selection of monitoring sites along Upper Silver and Coyote Creeks........ 11
Table 2. Water quality parameters surveyed in stream, groundwater, and recycled water. 14
Table 3. Summary of Analytical Methods........ 18
Table 4. Detection of two pharmaceuticals in recycled water........ 20
Table 5. Detection of caffeine in three sites along Silver and Coyote Creek in July of 2005........ 20
Table 6. Concentration of oxadiazon found at Silver Creek sites in July 2005 surface water........ 22
Table 7. Summary of trace organics compounds analyzed in May 2006, with the exception of PFCs which are shown in Table 10........ 23
Table 8. Concentrations of NDMA for baseline 2005 study.. 25
Table 9. Perfluorochemical concentrations (ng/L) for the baseline 2005 study, also showing the detection limits applicable to each sample set........ 26
Table 10. Perfluorochemicals[a] (ngl^{-1}) in Upper Silver and Coyote Creeks monitored during the dry months of 2006 and 2007........ 27
Table 11. Summary of PFCs detected in project recycled water in 2005-2007. 28
Table 12. Summary report of pharmaceuticals, hormones, APEMs, and other compounds monitored as part of the 2005 baseline study of the Yerba Buena Pump Station recycled water, Silver and Coyote Creeks sites 1-6, and groundwater monitoring well 3 near Coyote Creek.. 31
Table 13. Summary of all analytes detected and not detected in the baseline 2005 characterization of recycled water, groundwater, and creek water........ 32
Table 14. Time to removal of NDMA for triplicate microcosms (M1, M2, and M3) containing surface water or surface water and sediment. 34

LIST OF FIGURES

Figure 1. Sampling locations proposed in the Jones & Stokes *Initial Study (Jones & Stokes, 2000).* 9

Figure 2. Aerial photograph of Upper Silver and Coyote Creeks with surface and groundwater sites shown. 10

Figure 3. Final selection of surface, groundwater, and hyporheic groundwater monitoring sites along Upper Silver and Coyote Creeks. 10

Figure 4. Perfluorochemicals monitored in the present study. 15

Figure 5. Concentrations of NBBS at all sites for three 2005 sampling events. 21

Figure 6. Tris(3-chloropropyl)phosphate concentrations for the baseline 2005 study. .. 21

Figure 7. Tris(2,3-dichloropropyl)phosphate concentrations for the baseline 2005 study. 22

Figure 8. Structures of several APEO metabolites (NPEC, CA_8PEC, NP, and a halogenated NP_2EC, respectively). 24

Figure 9. Concentration of APEMs in recycled water sampled during the baseline 2005 study. 24

Figure 10. Percentage contributions of 11 PFCs for average of surface water sites 1-6 in October 2005. 28

Figure 11. Percentage contributions of 10 PFCs for average of surface water sites 1-6 in November 2005. 29

Figure 12. Percentage contributions of 10 PFCs for average of recycled water in July, August, October, November 2005. 29

Figure 13. Total PFCs plotted with river mile along Upper Silver and Coyote Creeks. . 30

Figure 14. Average NDMA photodecay rate constants predicted for midday solar irradiance in mid-latitude and tropical zones in surface water with intermediate light screening and a depth of 1 m. 36

Figure 15. (A) NP1EC (log scale) and (B) CAP1EC concentrations as a function of time in the Coyote Creek microcosms (CCGB1 and CCGB2). 37

EXECUTIVE SUMMARY

Water agencies in the U.S. and elsewhere are expanding wastewater reclamation (or water reuse) as part of their water supply portfolio to meet the needs of growing populations. Recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. The re-used water must be protective of both stream ecology and groundwater, and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed.

Water recycling for environmental applications requires consideration of a complex set of benefits and risks. Wastewater may contain trace levels of organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although water reuse is generally regarded as a sustainable approach to water supply management, the presence of trace organic contaminants raises concerns about the use of this water in applications such as environmental enhancement.

The goals of the present study were to augment Coyote Creek in San Jose, CA with local recycled water as a research demonstration and to assess any potential impacts to water quality. It was hypothesized that potential impacts of wastewater-derived organic contaminants may be mitigated by significant natural attenuation of those compounds at the site. The overall project approach was divided into two components – the field site assessment and laboratory investigation of contaminant fate. Field site assessment included the selection of water quality constituents, their analytical method development, and sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer tests. The laboratory investigation of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants. Additional objectives included the assessment of contaminant fate during percolation from Coyote Creek into groundwater under stream flow augmentation conditions and evaluation of appropriate pretreatment methods for the augmentation water if results indicated adverse effects on groundwater or stream ecology.

The assessment of the microconstituent risk associated with augmenting an urban stream with recycled wastewater is complicated by the fact that different constituents may be present in different concentrations in each water source. In this project, the water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as *N*-nitrosodimethylamine (NDMA) and alkylphenol polyethoxylate metabolites (APEMs). Some constituents were present in both, such as perfluorochemicals (PFCs), organophosphates, and *N*-butylbenzene sulfonamide (NBBS).

Though there was no known wastewater discharge into Upper Silver and Coyote Creeks, PFCs were found in the surface water and underlying groundwater at concentrations that were similar to the wastewater, highlighting the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement. As expected from their occurrence in wastewater and persistence during wastewater treatment, PFCs were also detected in the recycled water from the San Jose/Santa Clara Water Pollution Control Plant intended for the stream augmentation. Concentrations of total PFCs ranged 350-587 ng/l. Concentrations of perfluorooctanoic acoid (PFOA) and perfluorooctane sulfonate (PFOS) ranged 83-180 and 190-374 ng/l, respectively. While many PFC monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other PFCs in the monitoring program may identify several additional PFCs resulting in a much greater total PFC concentration.

With respect to ecotoxicological effects, PFC release via recycled water into sensitive ecosystems requires evaluation. PFCs bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal exposure which may be more ecotoxicologically relevant than the aquatic PFC concentration. The recycled water and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is protective of upper trophic level avian species that consume organisms in equilibrium with the water.

The laboratory investigation of NDMA fate showed that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. Biotransformation of NDMA is not likely to be a significant process during river and groundwater transport in the Upper Silver Creek and Coyote Creek system. However, NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight. Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines. Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively. Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be the most significant attenuation process even at relatively low levels of solar irradiation ($t_{1/2}$ = 8-38 h at 244-855 W/m^2, 51° N latitude, 1 m depth).

In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA. Final degradation products of the indirect photolysis of the perfluorooctanesulfonamides were PFOA and FOSA, which did not undergo additional degradation. A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed and includes oxidation and *N*-dealkylation steps. Given the slow rates expected for biodegradation and limited sorption, indirect photolysis of PFCs may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the creek study reach. Some transformation may be possible during additional travel time to San

Francisco Bay, depending upon the sunlight irradiation and reactive intermediates available to facilitate indirect photolysis of PFCs.

Biotransformation of the metabolites of alkylphenol ethoxylates (APEMs) was also assessed. Based on this study, significant biotransformation of APEMs could be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater. However, literature research suggests that under aerobic conditions, relatively stable APECs may be formed. Under anaerobic conditions, biodegradation may continue to form alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur. Water quality monitoring of the surface and groundwater following stream flow augmentation with recycled water would be required to fully assess whether concentrations of APEMs, if detected, were significant following the expected attenuation and dilution with site water.

Advanced treatment options are available for the removal of NDMA and PFCs in wastewater. In a laboratory study of the removal of PFCs by nanofiltration, rejections greater than 95% were measured for most PFCs tested and depended upon the solution pH (which controls the protonation state of the PFC) and the fouling layer. If nanofiltration or reverse osmosis were viable treatment options for wastewater prior to use in stream flow augmentation, these advanced treatment processes would result in adequate removal of PFCs.

As suggested by results obtained in a separate study for an advanced wastewater treatment facility at the time of this project, microfiltration (MF) of wastewater effluent is not expected to reduce NDMA concentrations and may in fact lead to NDMA formation when in combination with chlorination or chloramination used to prevent MF membrane fouling. However, reverse osmosis (RO) treatment of secondary effluent using thin-film composite membranes typically results in NDMA rejection of approximately 50 to 65% or less. For the overall treatment train, this rejection is an important contribution to NDMA removal. Lower rejection may be associated with changing feed conditions and fouling observed in real treatment systems. Thus, if RO was a viable treatment option for wastewater prior to use in stream flow augmentation, this advanced treatment process would likely result in a significant, though incomplete, removal of NDMA. UV irradiation in combination with RO treatment and in some cases, blending, may allow operators to reliably maintain the residual NDMA below the 10 ng/L CA drinking water notification level.

Abstract

Water recycling for environmental applications requires consideration of a complex set of benefits and risks. The goals of the present study were to augment Coyote Creek in San Jose, CA with local recycled water as a research demonstration and to assess any potential impacts to water quality. Field site assessment included the selection of water quality constituents and sampling campaigns of recycled water and site water. Laboratory investigations of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants. Results showed that water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as *N*-nitrosodimethylamine (NDMA) and alkylphenol polyethoxylate metabolites (APEMs). Some constituents were present in both water sources, such as perfluorochemicals (PFCs), organophosphates, and *N*-butylbenzene sulfonamide (NBBS). The recycled water and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is protective of upper trophic level avian species that consume organisms in equilibrium with the water. Laboratory investigations showed that NDMA is poorly degradable biologically but aquatic photolysis may be a significant attenuation mechanism. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for other nitrosamines. In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. However, rates of indirect photolysis for PFCs were quite slow, and thus significant rates of transformation would not be expected over the creek study reach. Biotransformation of the metabolites of alkylphenol ethoxylates (APEMs) was also assessed and could be expected at the Coyote Creek site upon infiltration of water the hyporheic and subsurface zones. In a laboratory study of the removal of PFCs by nanofiltration, rejections greater than 95% were measured for most PFCs tested. Reverse osmosis (RO) results in NDMA rejection of approximately 50 to 65% or less. For the overall treatment train, this rejection is an important contribution to NDMA removal.

Keywords: water reuse, wastewater reclamation, emerging contaminants, NDMA, perfluorochemicals

1.0 INTRODUCTION

1.1 Overview

An increasing number of communities in California are turning towards water recycling as a means to meet the growing demand for water. The traditional solution to increase water supplies has been to import water from distant sources. However, this option has been vanishing with population growth spreading all across the Southwest. In cases where human uses have diminished the water source that an ecosystem depends on, one option is to treat impaired sources—including tertiary effluents—such that the treated water can replenish the water source. Water agencies in the U.S. and elsewhere are expanding wastewater reclamation (or water reuse) as part of their water supply portfolio to meet the needs of growing populations.

Recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. The re-used water must be protective of both stream ecology and groundwater, and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed.

Although the release of treated wastewater to surface water has historically been commonplace given the lack of alternatives, water recycling nevertheless requires consideration of a complex set of benefits and risks at sites where a natural source (rain, groundwater, rivers) is replaced or augmented with tertiary effluent. Wastewater may contain trace levels of organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. The identification of these compounds in wastewater or the receiving water body depends on 1) the application of analytical methods to specifically target the desired compound or compounds and 2) the detection limits of the analytical method. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although water reuse is generally regarded as a sustainable approach to water supply management, the presence of trace organic contaminants raises concerns about the use of this water in applications such as environmental enhancement.

1.2 Background

The City of San José previously proposed to augment stream flow in Coyote Creek by up to 400% with recycled water. Several relevant supporting studies were conducted for the City. Chief amongst these studies was the “Revised Initial Study” (2000), which evaluated the ecological and groundwater impacts of the augmentation. A primary objective of the San José scheme was to improve cold-water habitat in Coyote Creek, thus recycled water was to be dechlorinated and chilled significantly prior to release into the creek. For groundwater, the study noted that the Santa Clara groundwater basin, which contains the reach of Coyote Creek to be studied, is divided into three zones: a shallow unconfined aquifer, a regional aquitard, and beneath the aquitard a potable deep confined aquifer. Considering the location of the City’s proposed outfall at

Singleton Landfill, recycled water in Coyote Creek would only flow over the regional aquitard and infiltration to the potable deep aquifer would be unlikely. The report noted that there is a low probability of infiltration to the shallow aquifer due to the clayey composition of the creek bottom; nevertheless, monitoring of shallow aquifer water quality was recommended to confirm that no recharge with recycled water was taking place.

Another concern that arose during the City of San José project was the degradation of water quality due to trace organics and endocrine disruptors. The appearance of these compounds in the aquatic environment is a recent environmental concern because some of them are biologically active and viewed as potentially harmful to wildlife and human health.

In late October 2000, the City of San José obtained a permit from the California Regional Water Quality Control Board (RWQCB) to implement a demonstration stream flow augmentation project in Coyote Creek. The City decided not to proceed with the project and the RWQCB permit expired in June 2003.

1.3 Project Rationale

The central rationale for this project is that it increases the potential for the expanded use of recycled water by the Santa Clara Valley Water District (SCVWD) in Santa Clara County, which is consistent with the desires and policies of the District Board of Directors (Board). It also has the potential to provide augmented creek flows for environment benefit as part of the “Environmental Stewardship” mission of the Board.

As described in the original project work plan (SCVWD, 2004), it was also proposed that Stanford University (a project partner) would use the augmentation to test the central hypothesis that natural biological, physical, and chemical action during stream flow can improve the stream’s water quality via natural attenuation of trace organics. Likewise, natural action during the infiltration of surface water into groundwater can further improve the water quality of the infiltrating water. The natural attenuation of any microconstituents present in the reclaimed wastewater would thus mitigate impact of these constituents on the environment and reduce any potential impact on drinking water supplies.

The hypothesis was based upon prior studies conducted by Stanford University researchers. With support from the Orange County Water District, Reinhard et al. conducted a similar study of water quality changes in the Santa Ana River in Southern California (Reinhard et al., 1999; Reinhard and Ding, 2001). The Santa Ana River carries nearly 100 percent tertiary treated water during the summer months (Gross et al., 2004). In that study it was found that trace organic contaminants such as pharmaceuticals and alkylphenol ethoxylate metabolites (biological degradation products of nonionic detergents) are significantly attenuated during river transport suggesting that the river itself acts as an efficient treatment system. The subsequent infiltration of river water into the ground led to significant additional water quality improvement in terms of total organic carbon (dissolved and particulate) and trace organics.

1.4 Project Objectives

The original objective of this research-scale study was to augment the stream flow of Coyote Creek in San José using recycled water produced at the San José/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) and to examine any impacts upon the creek. As stated in the original project work plan (SCVWD, 2004),

> The overall goal of the stream augmentation project is *to assess the potential impact of large-scale augmentation of the Coyote Creek flow with tertiary treated water on the water quality of the river and the underlying groundwater. If results indicate adverse effects, appropriate treatment methods will be evaluated. These treatment methods may include Reverse Osmosis treatment, soil treatment, or blending with higher quality water.*

The source of Coyote Creek is located in the upper reaches of the Santa Clara Valley, and flows over 20 miles through suburban and urban areas to its mouth in South San Francisco Bay. The tertiary treated recycled water was to be released into the stream approximately 15 miles upstream from the Bay. The study originally proposed to add from 2 to 6 cfs of recycled water to Coyote Creek, corresponding to two to three times base summer flow (base flow readings are available at http://alert.valleywater.org/gagestrm.html). This augmentation plan was later amended to involve temperature monitoring and flow adjustment due to concerns about temperature impacts on the stream, resulting in an estimate that the recycled water addition would be equal to or less than the base summer flow. In 2007, the SCVWD drafted an Initial Study/Mitigated Negative Declaration (SCVWD, 2007) prepared in compliance with the California Environmental Quality Act (CEQA) and the State CEQA Guidelines (not finalized).

In the spring of 2008, SCVWD cancelled the augmentation due to concerns over the presence of perfluorochemicals in the recycled water intended for the augmentation. As described in the project work plan, microconstituents originally assessed in the wastewater and stream included pharmaceuticals. The list of target analytes was reassessed and compounds including perfluorochemicals were added and surveyed in the recycled water and at the site. Following detection of perfluorochemicals in the recycled water at concentrations typical of wastewater, a brief assessment of perfluorochemical ecotoxicity was performed by Stanford University (Plumlee et al., 2008a). Based on a review of this information, SCVWD made the decision to cancel the augmentation.

Listed below are the project objectives as presented in the original project work plan. Although several of the objectives were met using both laboratory and field work, some objectives could not be met entirely due to the fact that the creek flow was not augmented using recycled water and subsequent monitoring of surface and ground water quality could not be performed.

The objectives of this study were:

1. To assess the potential of fate mechanisms – including photochemical degradation, adsorption, and biotransformation – to remove specific contaminants from tertiary treated recycled water used for large-scale augmentation of stream flow in Coyote Creek. The specific contaminants targeted for this study were selected based upon the results of a detailed characterization of the tertiary treated recycled water.
2. To assess the fate of contaminants during percolation from Coyote Creek into groundwater under stream flow augmentation conditions.
3. To evaluate the hydrological conditions of the study site—specifically the interactions between surface flow and shallow and deep aquifers
4. To evaluate appropriate treatment methods for the augmentation water, if results indicate adverse effects on groundwater or stream ecology.

2.0 PROJECT APPROACH

The overall project approach was divided into two components – the field site assessment and laboratory investigation of contaminant fate. To summarize, field site assessment involved the selection of water quality constituents, including emerging contaminants, their analytical method development if necessary, and the sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer test. The laboratory investigation of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants. Details of the approach for each task are given below.

2.1 Site selection and hydrology

2.1.1 Surface water sampling sites and hydrology

The original creek location and surface water sampling sites were along Coyote Creek in San Jose, as shown in the Figure 1 map. Later, Upper Silver Creek (a tributary to Coyote Creek) was selected for discharge of the recycled water due to the creek's proximity to recycled water pipelines at the Yerba Buena pump station, as shown in the aerial photograph in Figure 2. Thus the surface water sampling sites were modified to include both creeks. The objective was to choose sampling locations that permitted the monitoring of water quality changes in the creeks as the water flowed from the augmentation outfall point. Sampling points were selected such that, ideally, there were no additions/diversions that changed the quality or quantity of water in Coyote Creek. Additionally, a control site upstream of the augmentation outfall was selected.

The final selected sampling sites are shown in Figure 3 and described in Table 1.

Grab samples of surface water were collected from these sites along Upper Silver Creek and Coyote Creek over a reach of approximately 5 km. Samples were obtained from these sites and from the nearby Yerba Buena pump station (recycled water) in San Jose, CA at intervals of approximately once per month during spring and summer months during 2004-2007 to establish baseline water quality conditions.

To characterize stream hydrology, a tracer test using rhodamine WT and bromide as well as installation of stream gauges were planned but not executed following cancellation of the augmentation with recycled water.

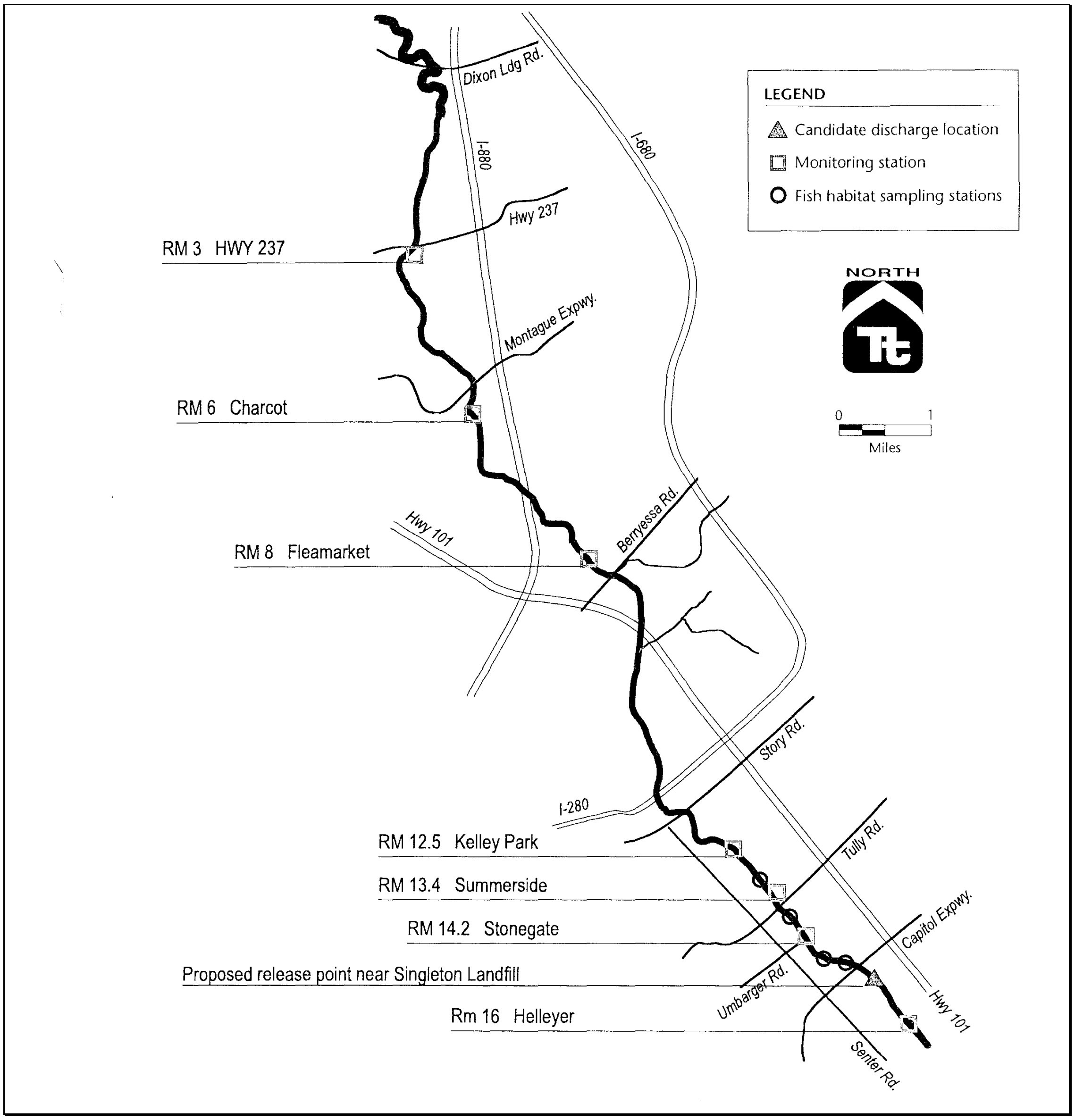

Figure 1. Sampling locations proposed in the Jones & Stokes *Initial Study (Jones & Stokes, 2000).*

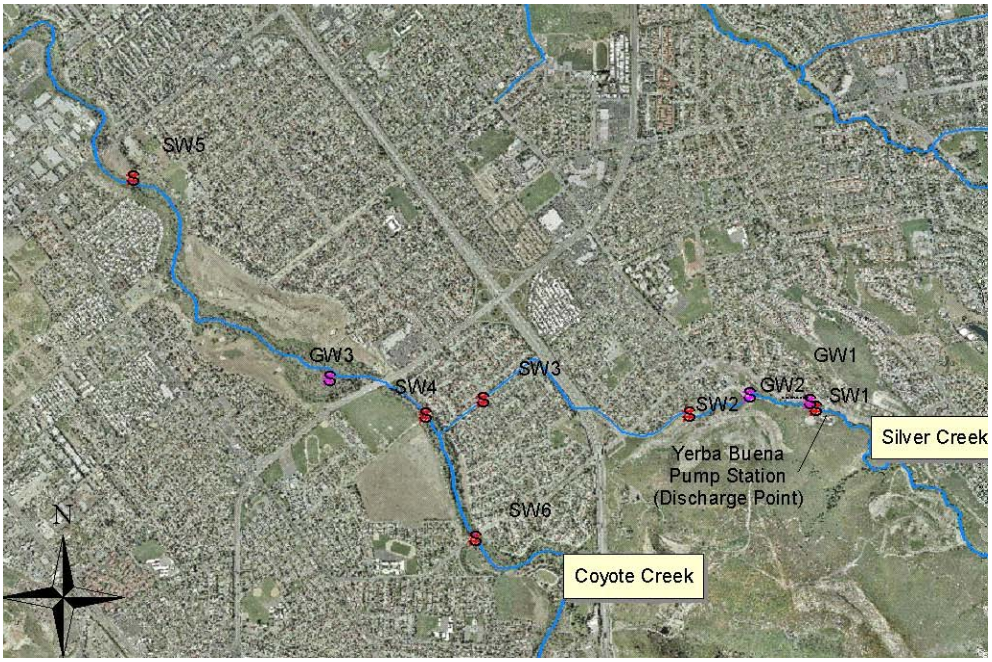

Figure 2. Aerial photograph of Upper Silver and Coyote Creeks with surface and groundwater sites shown. Creeks flow north.

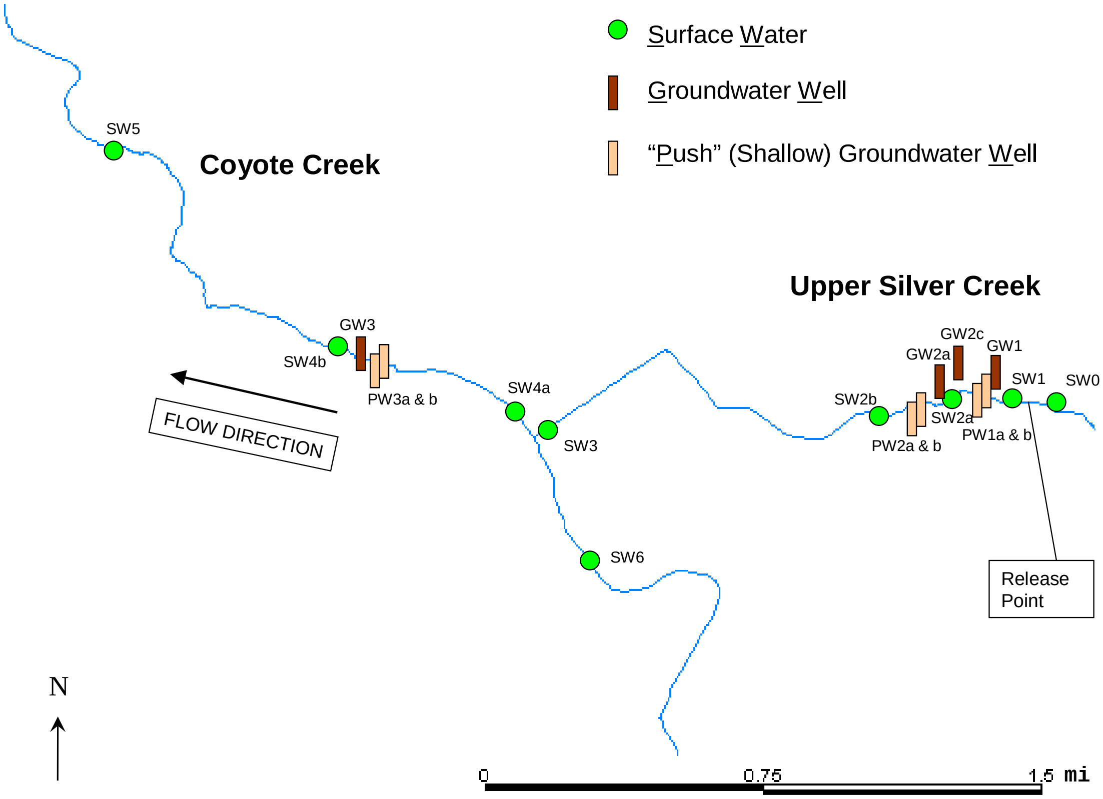

Figure 3. Final selection of surface, groundwater, and hyporheic groundwater monitoring sites along Upper Silver and Coyote Creeks.

Table 1. Description of sites from Figure 3, the final selection of monitoring sites along Upper Silver and Coyote Creeks.

SURFACE WATER SAMPLING POINTS:

Site Name	Description	Comment
SW0	0) Control site on Upper Silver Creek upstream of recycled water discharge	*site to be included following augmentation
SW1	1) Upper Silver Creek discharge point at Yerba Buena Pump Station	
SW2	2) Upper Silver Creek upstream of concrete channel	
SW3	3) Upper Silver Creek downstream of concrete Channel	
SW4	4) East bank of Coyote Creek near Singleton after Upper Silver Creek confluence	
SW5	5) Coyote Creek at Stonegate	
SW6	6) Coyote Creek control, at Yerba Buena Bridge upstream of confluence	
GROUNDWATER WELLS:		
Site Name	**Description**	
GW1	1) Near discharge point at Yerba Buena Pump Station	
GW2a	2a) near Upper Silver Creek at Silver Creek Line Park	
GW2c	2c) near Upper Silver Creek at Silver Creek Line Park	
GW3	3) After confluence near Coyote Creek	
"PUSH" WELLS (shallow, hyporheic zone wells):		
Site Name	**Description**	
PW1S PW1D	1) Slightly downstream of discharge point and GW1, in/near Upper Silver Creek bed	Shallow (2 ft) Deep (3 ft)
PW2S PW2D	2) At SW2, in Upper Silver Creek bed	
PW3S PW3D	3) Near GW3, in the Coyote Creek bed	
RECYCLED WATER:		
Site Name	**Description**	
RW1	1) Recycled water from SJ/SC WPCP at Yerba Buena Pump Station	

2.1.2 Installation of groundwater wells

In addition to surface water sampling along Upper Silver and Coyote Creeks, groundwater wells were installed adjacent to the creek and sampled during the baseline phase to establish initial conditions, with the intention to monitor the wells every month for one year during augmentation to determine whether target compounds in the recycled water impacted groundwater quality. Groundwater samples were obtained from four monitoring wells (Figure 3; GW1, 2a, 2c, and 3) installed to depths of 5-10 m. Depth-to-water ranged 2-5 m for the four wells. Additional plans for augmentation which were not carried out due to the cancellation were to monitor water quality in the infiltration flow path so that contaminant attenuation could be assessed as a function of distance and residence time.

In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells.

Further descriptions of site hydrogeology determined from historical records or field investigations employed in this project, including the use of temperature and radon as groundwater tracers, may be found in a separate report given in Appendix B.

2.1.3 Hyporheic zone

In addition to the installation of traditional groundwater wells, very shallow groundwater wells were installed in the creek bed at a depth of just 0.6-0.9 m to capture young groundwater in the hyporheic zone, a region in which surface and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). These "push wells" (PW1, 2, and 3) were installed in or adjacent to the creek. More details may be found in Appendix B.

2.2 Characterization of water quality

2.2.1 Selection of target analytes

As a preliminary task, project personnel screened the recycled water and stream sites for a range of trace organics shown below (Table 2), and then made a final selection of those compounds detected regularly and/or in sufficient quantities to include in future monitoring. Analysis of the trace organics, including some emerging contaminants, was performed by Stanford University personnel.

In addition, SCVWD performed additional analysis for a number of compounds listed in Table 2, including metals, disinfection byproducts, and microorganisms.

On-site and general water quality parameters, such as pH, dissolved oxygen (DO), dissolved organic carbon (DOC), anions, etc. were also included and performed by both Stanford and SCVWD personnel depending on the campaign.

Water quality assessment of the stream, groundwater, and recycled water was performed to establish baseline conditions prior to augmentation. Monitoring campaigns of this type were executed, typically in the spring and summer months, during 2004, 2005, 2006, and 2007. These campaigns were carried out each year in preparation for augmentation planned to occur that summer, but each year the augmentation was postponed to the next year for various reasons (namely construction and/or permitting delays). The target analytes and particular field sites included each year varied slightly as the project focus and available analytical methods were refined.

Of particular concern to this study were organic contaminants that may occur at trace concentrations, commonly referred to as "trace organics" or "microconstituents". These may include "emerging contaminants," or microconstituents for which toxicological information is sparse and official water quality criteria (for drinking or wastewater) have not been established.

Trace organics surveyed in this project included pharmaceuticals (such as gemfibrozil, ibuprofen, naproxen, ketoprofen, carbamazepine), hormones (estrone, 17α-ethynyl estradiol, 17β-estradiol, estriol), the metabolites of alkylphenol polyethoxylates (APEMs), N-butyl benzenesulfonamide (NBBS), chlorinated tris-propylphosphates (TCPPs), N-nitrosodimethylamine (NDMA), and several perfluorochemicals (PFCs). The APEMs include alkylphenols (APs), short-chain alkylphenol polyethoxylates (APEOs), alkylphenol polyethoxycarboxylates (APECs) and carboxylated alkylphenol polyethoxycarboxylates (CAPECs).

Previous studies (March, June and July 2002) showed the presence of halogenated APEMs in SJ/SC WPCP effluents. Chlorinated APs and APEOs as well as chlorinated and brominated APECS were detected at concentrations up to 15 μg/L. These halogenated compounds are probably formed during chlorine disinfection in the presence of bromide. *All* other target compounds might also be present as halogenated derivatives, but if no commercial standards are available, no analytical methods are available.

NDMA and PFCs were added to the list of target compounds when the pharmaceuticals and hormones were not detected or were only detected intermittently, and because these compounds are of particular environmental concern because of their low maximum contaminant limit (NDMA) or ecological significance (PFCs). A list and structures of PFCs monitored in the present study is presented in Figure 4. More details on the environmental occurrence and toxicology of these compounds may be found in Appendices C and D (NDMA) and Appendix E and F (PFCs).

Table 2. Water quality parameters surveyed in stream, groundwater, and recycled water.

Fire Retardants	**2**
Tris (3-chloropropyl) phosphate	
Tris (2,3-dichloropropyl) phosphate	
Plasticizers	**2**
Bisphenol A	
N-butyl benzenesulfonamide	
APEMs	**4 groups**
Halogenated/Chlorinated APEMs	
APEOs	
Alkylphenols (nonyl-, octyl-)	
APECs, CAPECs	
NDMA (Disinfection Byproduct)	**1**
Perfluorochemicals	**11**

Organic Compounds	
Herbicides and Pesticides	9
Trihalomethanes	5
Haloacetic Acids	7
Metals	**19**
Microbes	**3 groups**
General Water Quality	**10**
On-site Parameters	**4**
Temperature, pH, Conductivity,	
Dissolved Oxygen	

Pharmaceuticals	**11**
Acetaminophen	
Caffeine	
Carbamazepine	
Carisoprodol	
Gemfibrozil	
Ibuprofen	
Iminostilbene	
Ketoprofen	
Naproxen	
Primidone	
Propanolol	
Hormones	**4**
Estradiol	
Estriol	
Estrone	
Ethynylestradiol	

Figure 4. Perfluorochemicals monitored in the present study.

2.2.2 Analytical methods

The analytical method (sample preparation and instrumental analysis) depended upon the target analyte. The analytical methods utilized for microconstituent analysis by Stanford University personnel are described here and summarized in Table 3. Method detection limits, where known, are reported with the results.

Pharmaceuticals, hormones, organophosphates, plasticizers, oxadiazon, and APEMs (analyzed together)

For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. To recycled water, 1 mL of a sodium thiosulfate solution was added to quench chlorination. Following return to the Stanford laboratory, samples were stored at 4°C.

For analysis (Gross et al., 2004; Lin et al., 2006), liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 μm nylon filters and adjusted to pH 2.3. A blank of Milli-Q purified water was also prepared. C-18 cartridges with 1.0 g sorbent (Alltech, IL, USA, extract-clean columns, 8 mL) for the May analysis, C-18 with 2.0 g sorbent for the July analysis, and phenyl cartridges with 1.0 g sorbent (Phenomenex Strata End-Capped, 6 mL) for the August analysis were used to extract the target contaminants from 1 L samples by solid phase extraction (SPE). Each site was analyzed in replicate. SPE was performed using a 16-port vacuum extraction manifold. Cartridges were conditioned sequentially with 6 mL acetone, 6 mL acetonitrile, and 10 mL Milli-Q water (pH 2). The samples were then loaded through the cartridges by applying a vacuum at a flow rate of 10 mL/min or less. The cartridges were then washed with Milli-Q water and dried under vacuum. Analytes were eluted with 5 mL acetonitrile followed by 5 mL acetone.

The extract was concentrated by evaporation on a sand block at 30-40ºC to 30-50 μL and divided into two or three fractions. To one fraction, 10 μL of a 20 mg/L internal standard solution (chrysene-d_{12}) was added for neutral compounds analysis (some APEMs, some pharmaceuticals, oxadiazon, NBBS, BPA, and organophosphates). The second aliquot was used to analyze for acidic compounds (carboxylated APEMs, some pharmaceuticals). In this aliquot, carboxylic acids were converted into their respective propyl esters by adding 10 μL of 90/10 (v/v) *n*-propanol/acetylchloride to the evaporated samples and heating for 1 hour at 85ºC. After propylation, the samples were evaporated to near dryness and 10 μL of the chrysene-d_{12} internal standard solution was added. If the third fraction (for hormones, BPA, and some pharmaceuticals) was prepared, it was similarly derivatized but by silylation using 10 μl of MTBSTFA and heated for 3 hours at 95ºC, followed by internal standard addition.

Quantitation was performed by gas chromatography-mass spectrometry (GC-MS) by sample injection onto an Agilent 6890N GC with a 5973 MSD. A DB-5 capillary column (30 m x 0.32 mm I.D., film thickness 0.25 μm; Agilent, Wilmington, DE, USA) or an equivalent column was employed using helium as the carrier gas.

All analytes in the neutral and propylated fractions were monitored in the total ion current (TIC) mode (mass range m/z = 50 – 550; scan time 0.5 s) and quantified using their base ions. Compounds in the silylated fraction were monitored using single-ion monitoring (SIM) mode of their base ions. Since APs, APEOs, APECs, and CAPECs occur as complex mixtures, the different isomers are manually differentiated with respect to the number of ethoxy groups and the length of their alkyl-chain (i.e., octyl or nonyl). APECs and CAPECs, which produce many of the same mass spectral fragments, are generally reported as the sum of the APECs and CAPECs (denoted as A+CAPECs). Because no commercial standards were available for tris(3-chloropropyl)phosphate or some of the pharmaceuticals including iminostilbene, these compounds were tentatively identified in the samples by comparing the spectral characteristics of the sample peak with spectral characteristics in the NIST (National Institute of Standards and Technology) mass spectral library.

Concentrations of the individual compounds were determined *semi-quantitatively* by comparing the base ion with the m/z 240 ion of the internal standard, chrysene-d_{12}.

Thus, all reported concentrations are based on the assumption that the response factors for the internal standard and the analyte are the same.

N-Nitrosodimethylamine (NDMA)

An analytical method for NDMA in wastewater and surface water was developed for this project and is summarized here; it is also available in the publication included as Appendix C (Plumlee et al., 2008b). For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. Following return to the Stanford laboratory later the same day of collection, samples were stored at 4°C. For analysis, liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 or 0.45 μm nylon filters. A blank of Milli-Q purified water was also prepared.

NDMA was extracted from 500 mL or 1 L of sample water (each site analyzed in replicate) by solid phase extraction (SPE) with a 16-port vacuum extraction manifold using reservoirs packed with activated charcoal. Activated charcoal was washed with Milli-Q water at the same pH as the sample, dried overnight at 110ºC, and 1.0 g was packed into empty 8 mL SPE reservoirs fitted with a frit and filter at the base. The sorbent was wetted with Milli-Q water before loading the water sample under vacuum at a flow rate less than 5 mL/min. After loading the water sample, the bottles were rinsed three times with Milli-Q which served to wash the charcoal. The cartridges were drained except for a small amount of water left behind, which was eluted into 15 mL glass collection vials. NDMA was eluted from the charcoal using 2 mL acetonitrile (two times), 2 mL methanol (two times), and 2 mL acetone (two times). The extract was evaporated on a sand bath at 37ºC leaving 1-2 mL of solvent-free water. For instrumental analysis, the concentrated extracts following elution were returned to a pH of 5 – 9 by adding a small amount of concentrated NaOH. 0.3 mL of 110 ppb internal standard, NDMA-d6, was added to 1.0 mL of extract and stored at 4ºC until analysis.

NDMA was quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by injecting 50 μL at a flow rate of 0.15 ml/min onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). The instrument detection limit was typically 1 ppb and instrument reporting limit was 2 ppb NDMA, from which the method detection limit is 4 ng/L for 500 mL of loaded water sample.

Perfluorochemicals (PFCs)

An analytical method for PFCs in wastewater and surface water was adapted for this project from an available sediment method (Higgins et al., 2005) and is also available in the publication included as Appendix E (Plumlee et al., 2008a). To summarize, water samples of recycled, surface, and ground waters were collected (6 to 250 mL) in polypropylene bottles, after rinsing bottles three times with the sample water, and packed on ice in coolers until returned to the Stanford laboratory.

Each water sample was prepared for replicate analysis. Sample preparation involved the addition of a sample aliquot to a methanol-containing microcentrifuge tube, centrifugation, and transfer of the mixture to a vial containing a 70:30 (v/v) mixture of methanol and 0.01% aqueous ammonium hydroxide. An internal standard solution containing ^{13}C-labelled PFCs was added for quantitation.

PFCs were quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by large-volume injection of 490 μL onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). Calibration standards containing each of the 10-11 PFCs analyzed in the study were carefully matched in solution makeup to the sample preparation method, to minimize matrix effects and to achieve a linear calibration curve.

Table 3. Summary of Analytical Methods

Target Analyte	**Method**
On-Site Parameters Temperature Electrolytic Conductivity (E.C.) Dissolved Oxygen (D.O.) pH	Appropriate sensors
DOC	TOC Analyzer
Anions: nitrate, sulfate, etc	Ion Chromatography (IC)
Microconstituents	Gas Chromatography/ Mass Spectroscopy (GC/MS) or Liquid Chromatography/Tandem Mass Spectroscopy (LC/MS/MS)

2.3 Laboratory investigations of contaminant fate

Of particular interest in this project was the detection of NDMA and PFCs in the recycled water to be used for the stream flow augmentation of Upper Silver and Coyote Creeks. It was noteworthy, too, that PFCs were detected in the surface and groundwater at the site (as characterized during the baseline studies executed). Following a review of the pertinent literature, laboratory investigations of particular attenuation mechanisms for these compounds were carried out.

Specifically, rates of biodegradation of NDMA and APEMs were assessed using sediment and water collected from the site. Extensive testing of the photosensitivity of NDMA and PFCs to natural sunlight was also carried out. In adequately sunlit surface water systems, photochemical degradation may act in combination with biodegradation and sorption (and also volatilization and dilution) to naturally attenuate the concentrations of organic contaminants. Obviously, photolysis (via direct or indirect mechanisms) plays a particularly important role in the overall environmental fate of a trace organic compound when biodegradation and sorption are slow or negligible.

In some cases, photolysis may provide a reduction in the risk associated with the starting compound when the products of the reaction are harmless; in other cases, photolysis may result in transformation of the starting compound to a chemical or chemicals of concern. It is important to determine the identities of these products for a more complete evaluation of environmental fate and toxicity. Thus, product characterization was included in the photolysis studies of both NDMA and PFCs.

3.0 PROJECT OUTCOMES

3.1 Characterization of water quality

Presented below are the detections observed for each analyte or analyte group in all sample waters (recycled water from Yerba Buena pump station and surface and ground waters from Upper Silver and Coyote Creeks) and sites for the baseline characterization of 2005. The 2005 monitoring campaign included pharmaceuticals, hormones, organophosphates, plasticizers, APEMs, NDMA, and perfluorochemicals. Highlights are given in sections 3.1.1-3.1.4 and a more detailed data summary (detects and non-detects) is given in section 3.1.5.

A limited baseline water quality analysis was performed in May of 2006 for the same 2005 sites plus additional push wells and groundwater wells.

Prior to the last and final cancellation of the augmentation using recycled water, samples of the surface water, groundwater, and recycled water were collected in June of 2007. NDMA and perfluorochemical data analysis was completed and the results are presented here. Data analysis was not completed for the other trace organics upon cancellation of the augmentation.

Additional water quality analyses were performed in 2005-2007 by SCVWD. These data are presented in Appendix A and included the following water quality constituents: herbicides and pesticides; trihalomethanes; volatile organic compounds (VOCs); metals; haloacetic acids; microbes; and general water quality.

3.1.1 Pharmaceuticals, hormones, organophosphates, plasticizers and oxadiazon

No hormones and few pharmaceuticals were detected in much of the baseline 2005 study. Tables 4 and 5 show the detections of two pharmaceuticals, carisoprodol and iminostilbene, in the recycled water and caffeine in the creek water. In a previous investigation these same two pharmaceuticals were identified in the SJ/SC WPCP secondary effluent in June 2005. No other pharmaceuticals were detected in the recycled water. Note that all measurements only reflect the particular day and time sampled; pharmaceutical concentrations emitted in wastewater effluents may be quite variable even over a single day. One reason for the absence of many targeted compounds may be that the final effluent is chlorinated, which can oxidize many organics.

Caffeine was detected at three creek sites in 2005, spanning both Silver and Coyote Creeks. Caffeine has been demonstrated for use as a marker for wastewater contamination of surface waters (Buerge et al., 2003). The detection limits noted in the tables were determined from a statistical analysis of a calibration curve.

Table 4. Detection of two pharmaceuticals in recycled water. The detection limit of iminostilbene is not known as a standard was not available.

Recycled Water 2005	July	August	DL*
Carisoprodol (ng/L)	217	195	60
Iminostilbene (ng/L)	98	96	--
Carisoprodol: muscle relaxant, blocks pain			
Iminostilbene: intermediate in synthesis of analgesics and antipsychotic agents			

*DL: detection limit

Table 5. Detection of caffeine in three sites along Silver and Coyote Creek in July of 2005.

Surface Water July 2005	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	DL*
Caffeine (ng/L)	72	19	23	10
Caffeine: stimulant added to analgesics to enhance effect				

*DL: detection limit

NBBS, a plasticizer used in nylon production that is commonly found in US water bodies and is reportedly neurotoxic (Duffield et al., 1994), was found in recycled, creek and ground waters throughout the baseline 2005 study (Figure 5). Creek concentrations were generally similar to recycled water concentrations, with the exception of May when the creek levels at sites 3, 4, 5, and 6 were higher than the recycled water. A detection limit of 7 ng/L was determined based upon the statistical analysis of a calibration curve. NBBS was tentatively identified in July SW5 and August GW3 but concentrations fell below the limit of quantitification.

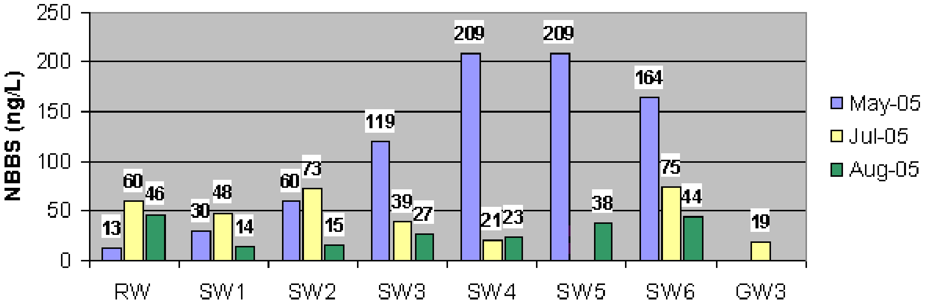

Figure 5. Concentrations of NBBS at all sites for three 2005 sampling events. Note that the groundwater well 3 was not sampled in May. Detection limit is 7 ng/L.

A single detection of BPA, 18 ng/L, was found in the July 2005 groundwater well 3 (GW3). BPA is a plasticizer used in polycarbonate plastic and epoxy resins and is considered estrogenic. The detection limit for this analyte has not been determined.

Results from the 2005 baseline monitoring for tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate, organophosphates used as fire retardants, are shown in Figure 6 and Figure 7, respectively. Both are on the EU priority list for carcinogenic suspicion. Tris(3-chloropropyl)phosphate (Figure 6) appears fairly consistently through most of the sampling sites except in the groundwater in August (not measured in May). Note the log scale; concentrations are much higher in the recycled water than in the natural waters, and are also higher in the creek than in the groundwater. Tris(2,3-dichloropropyl)phosphate (Figure 7) appears more sporadically, with a concentration on the order of μg/L noted in May surface water site 1. Because a standard was available for tris(2,3-dichloropropyl)phosphate, a detection limit of 10 ng/L was determined based upon the statistical analysis of a calibration curve.

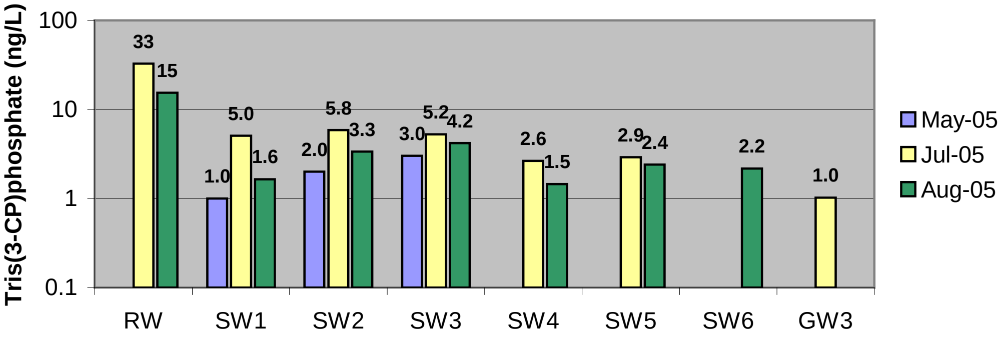

Figure 6. Tris(3-chloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit unknown (no standard available).

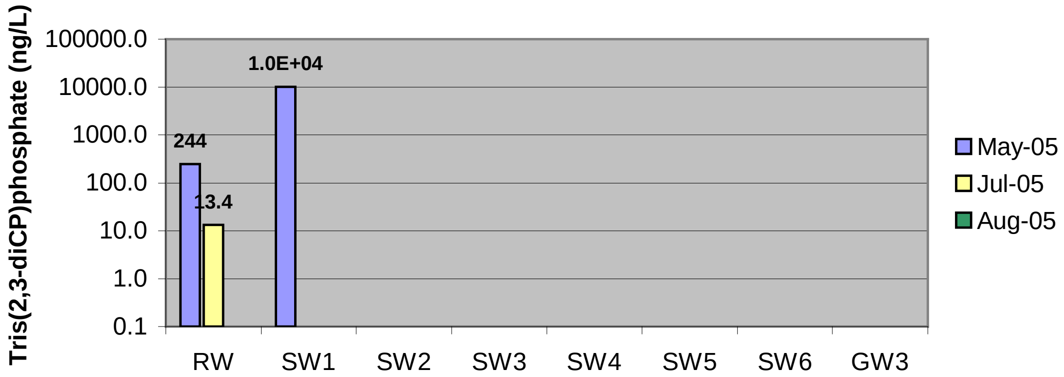

Figure 7. Tris(2,3-dichloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit is 10 ng/L.

The herbicide oxadiazon was added to the project analyte list after its discovery in preliminary analyses of the Coyote Creek surface water. It was not found in the recycled or ground water, and was only found in the surface water during the 2005 baseline study in one month (July) at the three sites on Silver Creek, as shown in Table 6.

Table 6. Concentration of oxadiazon found at Silver Creek sites in July 2005 surface water. Detection limits have not been determined.

Surface Water July 2005	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)
Oxadiazon (ng/L)	12	12	3
Oxadiazon: herbicide applied in CA (600 pounds in Santa Clara County, 2003 (www.pesticideinfo.org)); developmental/reproductive toxin, suspected carcinogen			

A limited baseline water quality analysis was performed in May of 2006 for the same 2005 sites plus additional push wells and groundwater wells. Some pharmaceuticals and the hormones were omitted from the analysis (those belonging to a step in the analysis in which compounds are derivatized by silylation), because previous data showed few or no pharmaceutical and hormone detections. To save time and expense, the *surface* water samples were not analyzed for pharmaceuticals and other trace organics once it was determined that the augmentation would not occur in 2006, and instead only the push and groundwater well samples were analyzed (as the 2005 data set for those sites is limited). The 2006 data is reported in Table 7.

Most notably, the pharmaceutical compounds carisoprodol and iminostilbene, as wells as *N*-butylbenzene sulfonamide (NBBS), the organophosphates, NDMA and PFCs were detected in the recycled water, which is consistent with 2005 data.

Table 7. Summary of trace organics compounds analyzed in May 2006, with the exception of PFCs which are shown in Table 10. Surface water samples were only analyzed for NDMA and PFCs.

Analytes	RW	PW1	PW2	GW1	GW2A	GW2C	GW3	SW1	SW2	SW3	SW4	SW5	SW6	BLANK
Pharmaceuticals (ng/L)														
Caffeine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Carisoprodol	**9**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Gemfibrozil	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Ibuprofen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Iminostilbene	**160**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Ketoprofen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Naproxen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
APEOs & APEMs (ng/L)														
Octylphenol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Others (ng/L)														
NBBS	**103**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
NDMA	**26**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tris(2,3-dichloropropyl)phosphate	**36**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Tris(3-chloropropyl)phosphate	**61**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Oxadiazon	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d

3.1.2 Alkylphenol ethoxylate metabolites (APEMs)

Figure 9 shows the results for summed metabolites of alkylphenol ethoxylates (APEMs), which are metabolites of nonionic surfactants, for the 2005 baseline water quality analysis. APEMs were excluded from the analysis, with the exception of octylphenol (Table 7). Example structures from this complex family of compounds are shown in Figure 8. Carboxylated APEMs (A+CAPECs: alkyl- and carboxyalkyl ethoxycarboxylates) and halogenated APEMs were detected in the recycled water each time it was sampled during the 2005 baseline study. Halogenated APEMs are chlorinated and brominated forms of the APEMs produced during wastewater disinfection. Halogenated APEMs made up 10, 19, and 5% of the total APEMs for May, July, and August 2005, respectively. Detection limits are largely unknown because pure standards are not available for most of these compounds; however the detection limit for individual APECs (and assumed to be the same for CAPECs) applied in this study is approximately 0.5 ng/L. No APEMs were detected in creek surface or ground waters.

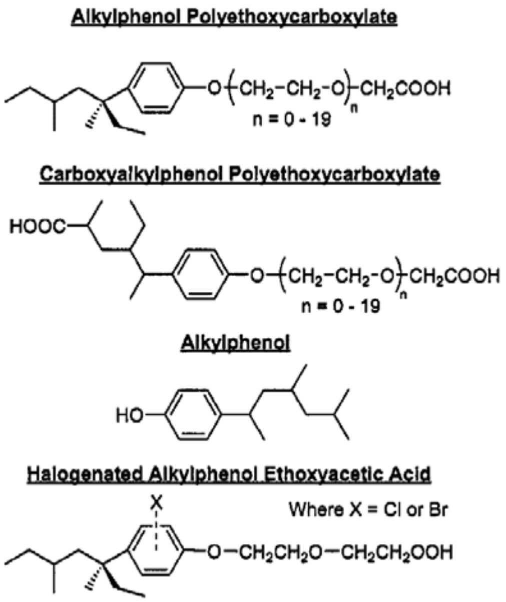

Figure 8. Structures of several APEO metabolites (NPEC, CA_8PEC, NP, and a halogenated NP_2EC, respectively). Reproduced from Montgomery-Brown and Reinhard (2003).

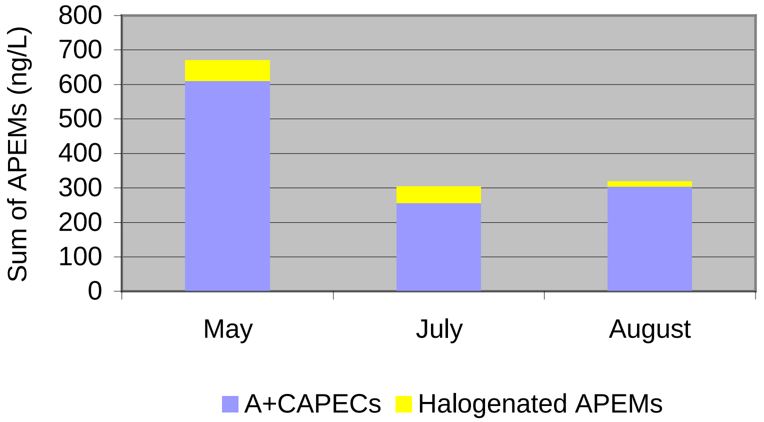

Figure 9. Concentration of APEMs in recycled water sampled during the baseline 2005 study. APEMs detected consisted entirely of A+CAPECs and halogenated APEMs.

3.1.3 N-Nitrosodimethylamine (NDMA)

NDMA is a disinfection byproduct formed during chloramination of waters containing dimethylamines and is considered a probable carcinogen. As shown in Table 8, NDMA was only found in the recycled water (all sampling events) and not found in the surface or ground waters during the 2005 baseline monitoring campaign. NDMA was also monitored during the May 2006 sampling campaign and was again detected in the recycled water (Table 7).

Table 8. Concentrations of NDMA for baseline 2005 study. Detection limit is 4 ng/L.

NDMA (ng/L)	RW	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	SW 6 (Coyote)
June	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
August	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
October	61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
November	111	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*DL: detection limit

In contrast to the 2005 and 2006 data, NDMA was not detected in the recycled wastewater collected in 2007. It is possible that the concentration of NDMA found in wastewater varies throughout the day, and that at the time of the June 2007 sampling event, the concentration was simply below the method detection limit (2 ng/L). In agreement with previous data, NDMA was not detected at any of the surface and groundwater sampling locations. This is expected since NDMA is a wastewater disinfection byproduct, and the stream sites did not receive any known wastewater discharge.

3.1.4 Perfluorochemicals (PFCs)

Perfluorochemicals have structures or substructures (carbon skeletons) that are fully fluorinated. PFCs are used for many purposes such as textile and paper coatings, fire fighting foams, and fluoropolymer manufacturing. They can be found in products from the commonly used brands/products Teflon, Scotchguard, Gore-Tex, and Stainmaster (Plumlee et al., 2008a). There are many persistent degradation products of which ten were chosen for this project because of their frequent occurrence in wastewaters and/or relevance to other research.

Table 9 gives a summary of the results from the 2005 baseline study (note, PFBS was eliminated from future analyses when it became undetectable after method modifications were made). The compounds were found in the recycled and surface waters, with higher concentrations (three to four times for the higher level PFCs) in the recycled water. The detection limits are shown with the data and vary slightly by compound and sample batch. Baseline concentrations of PFCs were reassessed in the spring of 2006 and again in 2007 when augmentation was postponed to these years. The 2006 and 2007 data for the field site (surface and groundwater) are presented in Table 10, showing results from additional groundwater and push wells installed after 2005. A summary of PFCs detected in the recycled water between 2005-2007 is given in Table 11.

Additionally, Table 9 shows a test of Teflon tubing compared to the groundwater well 3 October result. The groundwater was sampled with Teflon tubing, which is not recommended for perfluorochemical analysis but was carried out since perfluorochemicals were not considered during initial project planning. One to two months after sampling, the same Teflon tubing was obtained and rinsed with MQ water; one 60 mL sample in polypropylene was taken and analyzed for Perfluorochemicals in replicate. The results show that indeed some perfluorochemicals may originate from the tubing, including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA), but it is also likely that these ubiquitous chemicals were simply present in the MQ water. Of these, PFOS was detected in the groundwater (at approximately three times greater concentration). Additionally, PFHxS was detected in the groundwater and not in the tubing. PFOS should be considered a tentative groundwater identification since it was detected in the test of the Teflon tubing. These issues highlight some of the difficulties of perfluorochemical analysis.

Table 9. Perfluorochemical concentrations (ng/L) for the baseline 2005 study, also showing the detection limits applicable to each sample set. Additionally, results for the groundwater sample and test of the Teflon tubing used to sample the groundwater are shown. Sample names include site (RW = recycled water, SW = surface water) and date.

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	Total PFCs (ng/L)
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
RW_0705	Aug-05	50	20	341	7.7	n.d.	13	103	15	4.6	2.1	30	587
RW_0805	Aug-05	44	8	258	6.1	5.3	12	113	14	4.5	1.7	21	488
Blank_1005	Oct-05	n.d.	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	2.0
RW_1005	Oct-05	n.d.	7.9	160	n.d.	n.d.	n.d.	67	12	3.8	2.2	14	266
SW1_1005	Oct-05	n.d.	9.5	77	n.d.	n.d.	n.d.	27	3.7	7.3	4.3	n.d.	129
SW2_1005	Oct-05	n.d.	9.2	57	4.2	n.d.	8.2	26	3.2	4.3	5.2	7.2	124
SW3_1005	Oct-05	n.d.	9.2	62	n.d.	n.d.	n.d.	28	3.8	4.6	4.5	n.d.	112
SW4_1005	Oct-05	n.d.	1.7	12	n.d.	n.d.	n.d.	4.4	10	n.d.	n.d.	n.d.	28
SW5_1005	Oct-05	n.d.	2.1	15	n.d.	n.d.	n.d.	5.6	n.d.	n.d.	n.d.	4.9	28
SW6_1005	Oct-05	n.d.	n.d.	4.2	n.d.	n.d.	8.0	n.d.	n.d.	n.d.	n.d.	n.d.	12
Detection Limit	n/a	n/a	1.0	1.0	1.0	4.2	1.0	0.4	0.4	0.4	0.2	1.0	
Blank_1105	Nov-05	n.m.	n.d.	n.d.	1.9	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	1.7	4.2
RW_1105	Nov-05	n.m.	6.7	201	4.5	7.3	6.8	83	14	4.9	2.8	19	350
SW1_1105	Nov-05	n.m.	4.8	52	3.0	n.d.	4.3	19	2.4	5.1	2.4	2.5	95
SW2_1105	Nov-05	n.m.	4.5	50	3.9	n.d.	4.7	19	2.3	5.1	3.2	2.1	94
SW3_1105	Nov-05	n.m.	n.d.	67	5.1	n.d.	5.1	20	3.5	5.7	3.7	4.1	114
SW4_1105	Nov-05	n.m.	n.d.	7.3	n.d.	n.d.	n.d.	3.1	0.6	0.7	0.3	1.3	13
SW5_1105	Nov-05	n.m.	n.d.	7.2	2.7	n.d.	n.d.	3.1	1.1	0.8	0.6	3.2	19
SW6_1105	Nov-05	n.m.	n.d.	2.3	1.2	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	1.4	5.9

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	Total PFCs (ng/L)
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
GW3_1005	Nov-05	n.d.	8.4	26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	34
Teflon Test	Dec-05	n.m.	n.d.	8.4	n.d.	n.d.	n.d.	2.7	3.0	n.d.	n.d.	n.d.	14

Table 10. Perfluorochemicals[a] (ngl^{-1}) in Upper Silver and Coyote Creeks monitored during the dry months of 2006 and 2007. PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/l in May 2006 and 10 and 4 ng/l in June 2007, respectively. Sites are depicted in Figure 3.

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection Limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Creek water																
Site 1	n.d.	8.5 (1.0)	32 (11)	41 (8.3)	n.d.	36 (61)	n.d.	8.7 (1.5)	15 (0.8)	27 (10)	n.d.	11 (2)	n.d.	3.5 (0.6)	n.d.	10 (2.6)
Site 2a	n.m.	12 (1.1)	n.m.	45 (1.8)	n.m.	3.1 (0.1)	n.m.	10 (5.7)	n.m.	36 (0.7)	n.m.	12 (0.7)	n.m.	2.9 (0.3)	n.m.	5.7 (0.8)
Site 2b	n.d.	8.3 (0.5)	27 (5.7)	56 (30)	n.d.	11 (16)	n.d.	7.7 (0.8)	10 (0.4)	29 (2.3)	n.d.	19 (10)	n.d.	3.1 (0.6)	n.d.	n.d.
Site 3	n.d.	12 (2.0)	38 (4.8)	56 (4.4)	n.d.	6.3 (1.8)	n.d.	12 (1.2)	11 (0.5)	31 (6.2)	n.d.	19 (2.9)	n.d.	2.3 (0.3)	n.d.	6.1 (0.07)
Site 4	n.d.	3.8 (1.6)	14 (2.0)	25 (9.5)	n.d.	18 (15)	n.d.	4.7 (1.3)	n.d.	13 (5.2)	n.d.	13 (9.0)	n.d.	n.d.	n.d.	23.5 (24)
Site 5	n.d.	3.0 (1.2)	20 (0.8)	11 (7.3)	44 (0.0)	9.1 (6.4)	n.d.	3.2 (1.9)	n.d.	10 (6.0)	n.d.	6.0 (7.3)	n.d.	2.4 (0.2)	31 (2.1)	5.0 (0.6)
Site 6*	n.d.	2.3 (0.4)	9.3 (0.6)	4.8 (0.7)	n.d.	3.4 (1.2)	n.d.	n.d.	n.d.	8.0 (4.1)	n.d.	7.7 (2.1)	n.d.	n.d.	n.d.	n.d.
Hyporheic zone																
Push well 1	n.d.	n.m.	58 (3.7)	n.m.	n.d.	n.m.	n.d.	n.m.	23 (0.3)	n.m.	n.d.	n.m.	n.d.	n.m.	n.d.	n.m.
Push well 2	n.d.	10 (1.9)	44 (12)	48 (7.5)	n.d.	15 (0.7)	n.d.	8.1 (1.0)	10 (1.3)	28 (3.9)	n.d.	19 (2.4)	n.d.	4.3 (0.9)	n.d.	10 (0.6)
Push well 3	n.m.	3.8 (1.6)	n.m.	25 (9.5)	n.m.	5.7 (3.8)	n.m.	7.3 (0.9)	n.m.	22 (2.7)	n.m.	13 (1.2)	n.m.	2.9 (0.3)	n.m.	6.2 (0.3)
Groundwater																
Well 1	n.d.	8.9 (0.7)	85 (8.7)	40 (3.4)	n.d.	2.9 (1.3)	n.d.	n.d.	14 (5.9)	12 (1.6)	n.d.	7.3 (0.8)	n.d.	2.2 (0.2)	26 (18)	n.d.
Well 2a	n.d.	8.9 (4.2)	82 (1.1)	26 (4.8)	n.d.	n.d.	n.d.	4.8 (2.9)	22 (1.1)	18 (5.7)	n.d.	8.6 (2.6)	n.d.	n.d.	n.d.	n.d.
Well 2c	11 (3.8)	17 (3.5)	192 (33)	87 (5.3)	n.d.	3.3 (1.8)	n.d.	2.4 (0.6)	10 (0.6)	12 (1.6)	n.d.	10 (0.9)	n.d.	3.7 (0.7)	n.d.	n.d.
Well 3	9.2 (1.4)	4.0 (0.3)	31 (6.0)	19 (3.1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Mean (n=2) concentrations for creek water, hyporheic water, and groundwater. Range is given in parentheses.

Table 11. Summary of PFCs detected in project recycled water in 2005-2007.

San Jose/Santa Clara Water Pollution Control Plant Recycled Water [a]

Sample Date	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	*N*-EtFOSAA	Total PFCs
July 2005	20	341	7.7	13	113	15	4.6	n.d. (<4)	2.1	30	587
August 2005	8	258	6.1	12	103	14	4.5	5	1.7	21	488
November 2005	6.7	201	4.5	6.8	83	14	5	7.3	2.8	19	350
May 2006	n.d. (<4)	374	n.d. (<21)	5.4	120	9.5	n.d. (<21)	n.d. (<11)	n.d. (<21)	n.d. (<21)	508
June 2007	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470

[a] tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater

The contributions of different PFCs were calculated for the 2005 baseline study and is shown in Figure 10, Figure 11, and Figure 12. PFOS and PFOA make up the majority of the PFCs for both surface and recycled water. Perfluorobutanesulfonate (PFBS) and 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FtS) appear in the recycled water but not in the surface water (note, PFBS was not measured for November surface water). The pie charts represent an average of all measurements for the sites; levels of individual PFCs and distributions were quite consistent for both recycled and surface water.

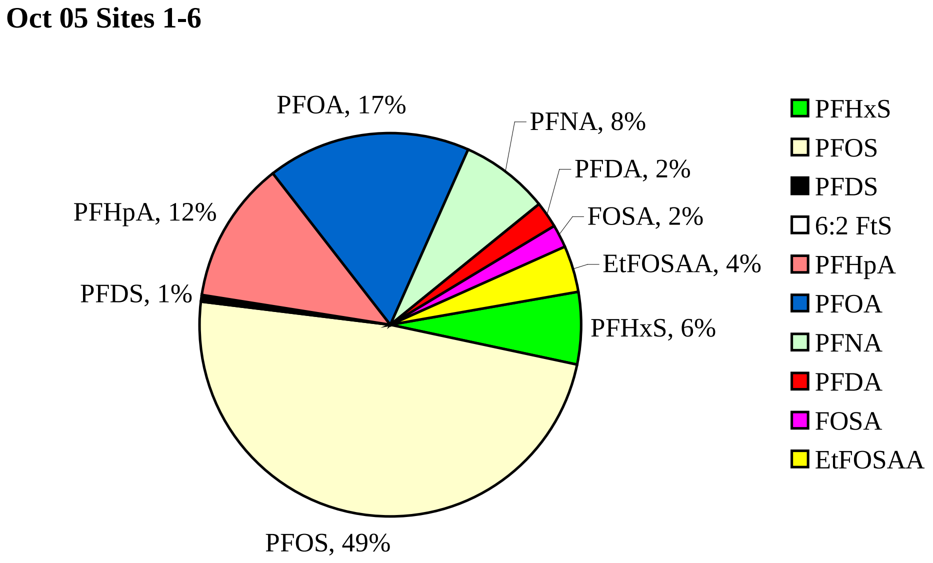

Figure 10. Percentage contributions of 11 PFCs for average of surface water sites 1-6 in October 2005.

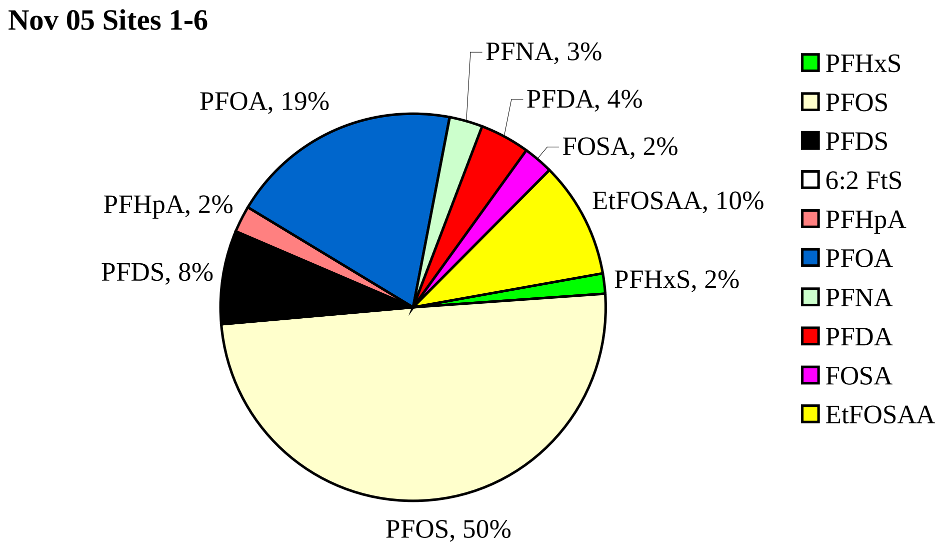

Figure 11. Percentage contributions of 10 PFCs for average of surface water sites 1-6 in November 2005.

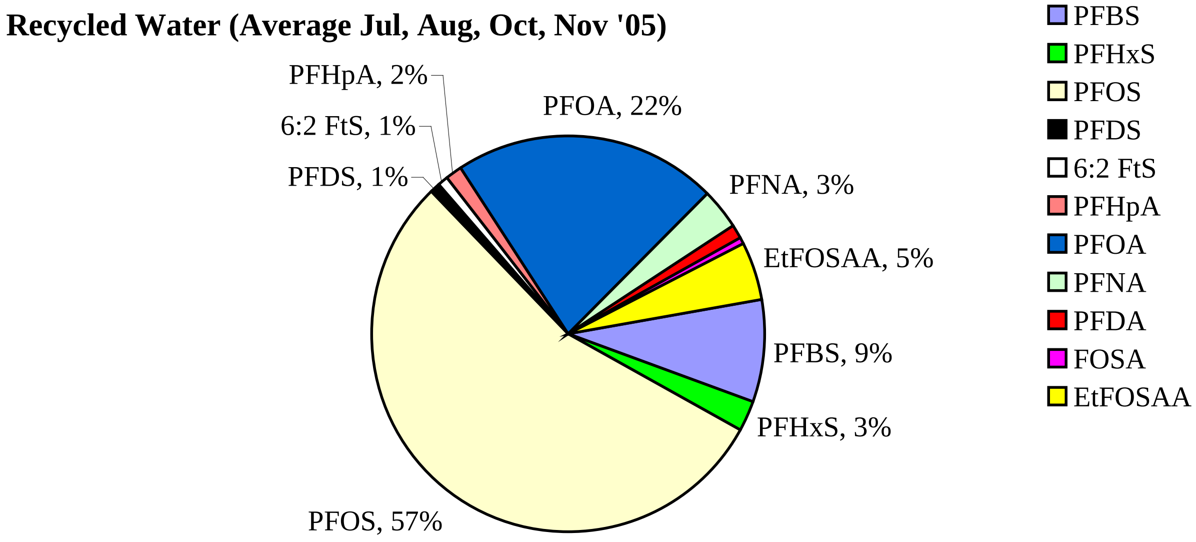

Figure 12. Percentage contributions of 10 PFCs for average of recycled water in July, August, October, November 2005.

Figure 13 shows the total PFCs plotted with distance along Upper Silver and Coyote creeks for October and November 2005. The results between the two months are consistent and show that Upper Silver Creek, the first three points, has higher levels of PFCs than Coyote creek, the lower three points. The result for the upstream control of Coyote Creek (Site 6, river mile 1.0) confirms that Coyote Creek has lower levels of

PFCs. Site 4 (river mile 1.7) is just downstream of the confluence of Silver and Coyote Creek, and shows the lower PFC levels that occur after mixing.

Further discussion of PFC occurrence, distribution, and comparison between recycled water and the creek system is provided in the publication presented in Appendix E.

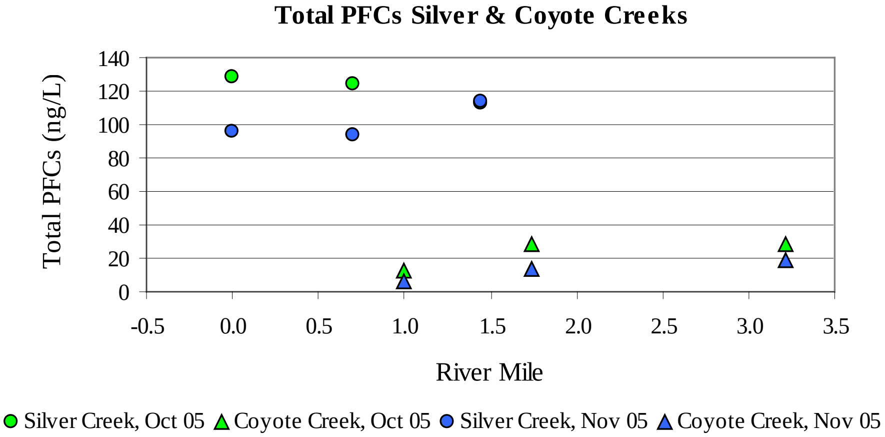

Figure 13. Total PFCs plotted with river mile along Upper Silver and Coyote Creeks. The green points indicate October 2005 results, the blue indicate November 2005 results.

3.1.5 Summary of 2005 baseline water quality study

Table 12 provides a summary of the baseline 2005 study analytical data for the recycled, surface, and ground waters at all dates and sites surveyed showing both the detections, non-detections (“n.d.”), and events in which certain analytes were not measured (“n.m.”). NDMA and PFCs are not included in this table as they were surveyed in slightly different months; these data may be found in Table 8 and Table 9, respectively.

Table 13 compares the creek system (surface and groundwater) to the recycled water by listing all analytes that were detected and not detected.

Table 12. Summary report of pharmaceuticals, hormones, APEMs, and other compounds monitored as part of the 2005 baseline study of the Yerba Buena Pump Station recycled water, Silver and Coyote Creeks sites 1-6, and groundwater monitoring well 3 near Coyote Creek. Sample sites are described in Table 1.

Analyte	**Yerba Buena Recycled Water**			**SW 1 (Silver Creek)**			**SW 2 (Silver Creek)**			**SW 3 (Silver Creek)**			**SW 4 (Coyote Creek)**			**SW 5 (Coyote Creek)**			**SW 6 (Coyote Creek)**			**Groundwater Well 3**		
	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05
Pharmaceuticals (ng/L)																								
Acetaminophen	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**72**	n.d.	n.d.	**19**	n.d.	n.d.	**23**	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carisoprodol	n.d.	**217**	**195**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Iminostilbene	n.d.	**98**	**96**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Primidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Propanolol	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Hormones (ng/L)																								
Estradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estriol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estrone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ethynylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
APEOs[1] & APEMs[2] (ng/L)																								
APEOs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Alkylphenols (nonyl-, octyl-)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
A+CAPECs[3]	**610**	**256**	**303**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Halog. APEMs[4]	**60**	**48**	**17**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Other (ng/L)																								
Bisphenol A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**18**	n.d.
N-butyl benzenesulfonamide	**13**	**60**	**46**	**30**	**48**	**14**	**60**	**73**	**15**	**119**	**39**	**27**	**209**	**21**	**23**	**209**	**<d.l.**	**38**	**164**	**75**	**44**	n.m.	**19**	**<d.l.**
Tris(3-chloropropyl)phosphate	n.d.	**33**	**15**	**1.0**	**5.0**	**1.6**	**2.0**	**5.8**	**3.3**	**3.0**	**5.2**	**4.2**	n.d.	**2.6**	**1.5**	n.d.	**2.9**	**2.4**	n.d.	n.d.	**2.2**	n.m.	**1.0**	n.d.
Tris(2,3-dichloropropyl)phosphate	**244**	**13.4**	n.d.	**1.0E+04**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**<d.l.**	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	**12**	n.d.	n.d.	**12**	n.d.	n.d.	**3.4**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.

[1] Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)

[2] Alkylphenol polyethoxylate metabolites

[3] Sum of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates (both metabolites of APEOs).

[4] Sum of halogenated (chlorine or bromine) alkylphenols, APEOs, and A+CAPECs

Table 13. Summary of all analytes detected and not detected in the baseline 2005 characterization of recycled water, groundwater, and creek water.

Recycled Water		Ground Water		Surface Water	
Found	**Not Found**	**Found**	**Not Found**	**Found**	**Not Found**
Carisoprodol	Acetaminophen	BPA	Caffeine	Caffeine	Acetaminophen
Iminostilbene	Caffeine	NBBS	Acetaminophen	NBBS	Carisoprodol
NDMA	Carbamazepine	Tris(3-chloropropyl)phosphate	Carisoprodol	Tris(3-chloropropyl)phosphate	Iminostilbene
		Tris(2,3-dichloropropyl)phosphate			
A+CAPECs	Gemfibrozil	PFCs	Iminostilbene	Tris(2,3-dichloropropyl)phosphate	Carbamazepine
Halog. APEMs	Ibuprofen		Carbamazepine	PFCs	Gemfibrozil
NBBS	Ketoprofen		Gemfibrozil		Ibuprofen
Tris(3-chloropropyl)phosphate	Naproxen		Ibuprofen		Ketoprofen
Tris(2,3-dichloropropyl)phosphate	Primidone		Ketoprofen		Naproxen
PFCs	Propanolol		Naproxen		Primidone
	Estradiol		Primidone		Propanolol
	Estriol		Propanolol		Estradiol
	Estrone		Estradiol		Estriol
	Ethynylestradiol		Estriol		Estrone
	BPA		Estrone		Ethynylestradiol
			Ethynylestradiol		NDMA
			NDMA		A+CAPECs
			A+CAPECs		Halog. APEMs
			Halog. APEMs		BPA

3.2 Assessment of PFC Occurrence and Toxicity in Wastewater and the Aquatic Environment

Following the detection of perfluorochemicals in the project recycled water as well as in the site stream and groundwater, and literature review of perfluorochemical occurrence and toxicity was conducted. The results are available in the publication presented in Appendix E (Plumlee et al., 2008a).

3.3 Characterization of site hydrology and hydrogeology

To characterize stream hydrology, a tracer test using rhodamine WT and bromide as well as installation of stream gauges were planned but not executed following cancellation of the augmentation with recycled water. The study originally proposed to add from 2 to 6 cfs of recycled water to Coyote Creek, corresponding to two to three times base summer flow of about 1 cfs. This augmentation plan was later amended to involve temperature monitoring and flow adjustment due to concerns about temperature impacts on the stream, resulting in an estimate that the recycled water addition would be equal to or less than the base summer flow.

Because possible infiltration of wastewater-derived microconstituents into the groundwater basin due to the augmentation was a concern, the hydrogeology of the system was considered. A more detailed discussion is provided in the separate report given in Appendix B. To summarize, it was concluded that if the creek feeds the hyporheic zone and underlying groundwater, sorption of contaminants to subsurface materials would enhance natural attenuation. A loss of creek water to riverbed and subsurface materials may, however, threaten the productive groundwater of the Santa Clara Valley basin. In the period between March and July 2006, the site was instrumented with i) three wells drilled at vertical distances of up to 50 *m* (160 *ft*) from the creek, ii) two wells pushed into the creek's bed (shallow "push wells"), and iii) temperature loggers in the creek and these wells. Additional push wells were installed later as depicted in Figure 3. The exploration of the site included i) an assessment of the hydraulic conductivity of subsurface materials, ii) a preliminary analysis of temperature time series, iii) an interpretation of an ongoing time series of water chemical analyses, and iv) radon water analyses. A tracer experiment with rhodamine WT and bromide was planned to complement the exploration work (though never executed once the augmentation was cancelled).

The existence of a hyporheic zone below the creek's bed was inferred from the temperature data. Flow from the creek's bed into shallow alluvial ground water could not be detected, although the ground water of the drilled wells is young and originates from the same catchment as the creek's water. It was concluded that contamination of the deeper productive aquifer with augmented water from the experimental site at Upper Silver Creek would not be probable. From the composition of the ground water in a well near Coyote Creek, which is similar to that of the creek itself, some downwelling of creek water was hypothesized. A tracer test would be required to gain insight into the mixing rates of recycled water with the various natural waters.

3.4 Laboratory investigations of contaminant fate

3.4.1 Biodegradation of NDMA

A laboratory study on the biological degradation of NDMA in sediment collected from Upper Silver Creek was performed. Details of the results and experimental approach may be found in the supporting information for the publication included as Appendix D (Plumlee and Reinhard, 2007); a summary is provided here.

Biodegradation of NDMA was observed in the microcosms containing either surface water alone or in combination with sediment (Table 14). Disappearance of NDMA (>80%) occurred more rapidly for the microcosms with sediment at 91-127 d, compared to 127-140 d in surface water. Constant NDMA concentrations in the sterile microcosms confirmed that NDMA was not lost via an unexpected pathway (e.g. volatilization, sorption to glass or septa) or via sorption to sediment, as expected from literature reports. As further evidence for biodegradation, the disappearance rate increased following the respike of the same microcosms (Table 14). This suggests the adaptation and growth of the microbial community, resulting in a greater biodegradation rate. The responsible microorganisms were not isolated; however, the degradation is likely to be cometabolic (Sharp et al., 2005; Yang et al., 2005). Bacteria having monooxygenase enzymes have been demonstrated to degrade NDMA (Sharp et al., 2005). If first-order kinetics are assumed, half-lives for NDMA biodegradation in microcosms with sediment and surface water were $t_{1/2} = 31\pm19$ (SD) d and decreased to 8±5 d following the respike. These rates are within the range of half-lives reported for NDMA biodegradation, from 4-6 d in groundcover and turfgrass soils (Yang et al., 2005), 11-39 d in soil slurries (Gunnison et al., 2000), to persistence in some soils and bog sediments (Tate and Alexander, 1976; Mallik and Tesfai, 1981).

Results show that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. The conclusion of this study is that biotransformation of NDMA is not likely to be a significant process during the residence times relevant to river and groundwater transport in the Upper Silver Creek and Coyote Creek system (hours to days).

Table 14. Time to removal of NDMA for triplicate microcosms (M1, M2, and M3) containing surface water or surface water and sediment.

Treatment	NDMA Addition (100 μg/l)	Time to ≥80% Removal, d M1	M2	M3	$t_{1/2}$ (SD), d
Surface Water (n=3)	Spike 1	127	140	140	67 (12)
	Spike 2	20	76	90	12 (13)
Surface Water + Sediment (n=3)	Spike 1	91	127	127	31 (19)
	Spike 2	20	20	34	8 (5)

3.4.2 Direct photolysis of NDMA

The photochemical degradation of photosensitive organic pollutants in the aquatic environment plays an important role in the overall environmental fate of these compounds. Because NDMA was detected in the recycled water to be used for the stream flow augmentation, and because wastewater treatment-focused studies had shown NDMA to be photosensitive, the aqueous photolysis of seven alkyl nitrosamines was studied by irradiation in a solar simulator. Nitrosamines included *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-n-propylamine (NDPA), *N*-nitrosodi-n-butylamine (NDBA), *N*-nitrosopiperidine (NPip), and *N*-nitrosopyrrolidine (NPyr).

Details of the experimental approach and a further discussion of the results may be found in the research publication included as Appendix D (Plumlee and Reinhard, 2007). To summarize, direct photolysis at irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines. Quantified products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively. Indirect photolysis of nitrosamines in surface water was not observed: increasing dissolved organic carbon (DOC) slowed the NDMA photolysis rate due to light screening.

Aquatic photolysis rates in real environmental systems may be different from laboratory measurements depending upon actual solar irradiance, the light screening by the water body of interest, and the water depth. However, if the quantum yield and molar absorptivity of the chemical are known, photolysis rates in the field can be estimated for the conditions of a particular site.

Figure 14 shows the average photodecay rate constant estimated for NDMA in a nonspecific surface water with a depth of 1 m and intermediate light screening by the water (spectral slope = 0.02 and $\lambda_{280} = 0.3$, (Green and Blough, 1994)). Midday solar irradiance was modeled using SMARTS for three locations representing a range of latitudes from January to December. The predicted rates shown in Figure 14 correspond to half-lives over the year of 8-38 h in London (51° N latitude), 7-14 h in Irvine (33° N latitude, the location of the OCWD site), and 6-7 h in Ecuador (2° S latitude). If the depth of the water body is reduced to 10 cm, the half-lives (corresponding to an average rate over the depth) are reduced by a factor of approximately 10. Thus for a typical river, depending upon the depth, solar irradiation, and light screening of the water, reaching an NDMA concentration attenuated by one half-life will require (sunlit) travel times of hours to a few days. This is consistent with a report by Pehlivanoglu-Mantas and Sedlak (Pehlivanoglu-Mantas and Sedlak, 2006) for the effluent-dominated Santa Ana River (CA, USA), in which a decrease in NDMA corresponding to approximately one half-life from the upstream wastewater treatment plant effluent (24 ng/L) to <10 ng/L downstream was observed after a 10 h residence time. Gross et al. (Gross et al., 2004) report the increased attenuation of trace organic contaminants for the same river compared to the nearby Prado Wetlands; given the reduced NDMA photolysis rate expected with increasing DOC via light screening (see Appendix D) and the greater DOC typically found for wetlands over rivers, shallow rivers may also be expected to outperform wetlands with regard to NDMA attenuation.

Because biodegradation is relatively slow, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2} = 8\text{-}38$ h at 244-855 W/m^2, 51° N latitude, 1 m depth). Based on the NDMA photodecay rates predicted in this study for a typical river, significant removal of NDMA by natural sunlight may be expected in Coyote Creek before it reaches San Francisco Bay, if recycled wastewater were to be added to this stream. However, over the short study area at Upper Silver and Coyote Creeks (Figure 3), the amount of NDMA attenuation observed would depend on light intensity and other site-specific conditions.

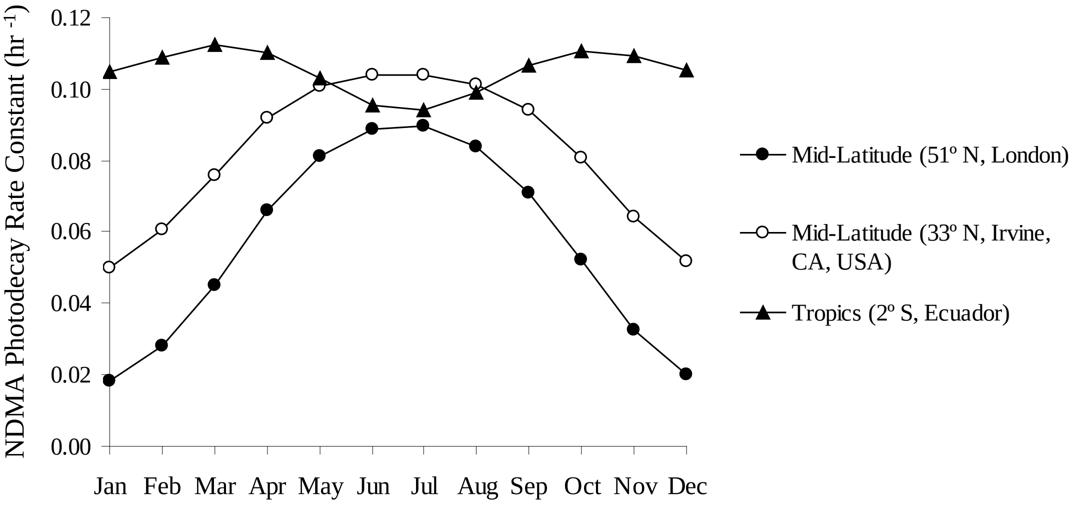

Figure 14. Average NDMA photodecay rate constants predicted for midday solar irradiance in mid-latitude and tropical zones in surface water with intermediate light screening and a depth of 1 m.

3.4.3 Biodegradation of APEMs

As described earlier in the report, metabolites of alkylphenol polyethoxylate compounds (APEMs; see Figure 8 for structures) were also detected in the recycled water intended for the stream flow augmentation. To explore the potential for degradation of these types of compounds by microorganisms in sediment from the site, a laboratory study on the biological degradation of nonylphenol ethoxyacetic acid (NP_1EC) in sediment collected from Coyote Creek was performed. Further details of the results and the experimental approach may be found in the publication included as Appendix G (Montgomery-Brown et al., 2008); a summary is provided here.

In this study, NP_1EC was spiked into oxic microcosms containing sediment from Coyote Creek and was monitored to evaluate the ability of this river to degrade NP_1EC. No degradation was observed under anaerobic conditions. The biological transformation pathway was elucidated by observing the appearance of products including dicarboxylated alklyphenol ethoxyacetic acids (CA_nP_1EC; where n = the number of aliphatic carbon atoms). Novel metabolites were observed that appeared to be specific to *ortho*-isomers (versus *para*-isomers) of NP_1EC. Results also suggested that dissolved oxygen availability was important in determining the dominant biodegradation pathway. Figure 15 shows the disappearance of NP_1EC over time in the spiked microcosms and the appearance of products. Overall, CA_8P_1ECs were the dominant metabolites of NP_1EC biodegradation initially, but CA_6P_1ECs became the dominant metabolites as biodegradation progressed.

Based on this study, significant biotransformation of APEMs may be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater.

Research available in the literature (Jonkers et al., 2001; Montgomery-Brown and Reinhard, 2003; Montgomery-Brown et al., 2008) shows that under aerobic conditions, relatively stable APECs (with one to three ethoxy units, i.e. AP_nECs where n = 1-3) may be formed. Under anaerobic conditions, biodegradation may continue to form alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur.

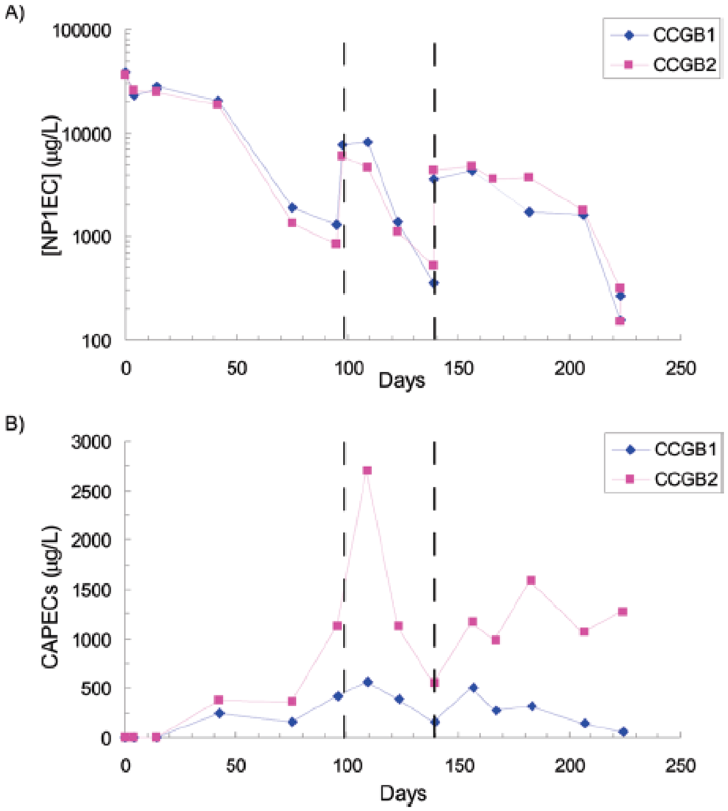

Figure 15. (A) NP1EC (log scale) and (B) CAP1EC concentrations as a function of time in the Coyote Creek microcosms (CCGB1 and CCGB2). Dashed lines indicate NP1EC respike events.

3.4.4 Indirect photolysis of PFCs

Because PFCs were detected in both the recycled water to be used for the augmentation and in the creek system, a laboratory investigation of PFC attenuation potential was carried out. The fluorinated portion of these compounds is generally regarded as extremely persistent, with disappearance of particular PFCs typically explained by transformation into a simpler PFC, such as PFOS or PFOA. Because biodegradation is expected to be quite slow and sorption to sediments may be negligible, attenuation by photolytic means was selected as the focus of the laboratory study. While research has suggested that PFCs are not susceptible to direct photolysis (transformation upon direct absorption of light), and this was confirmed in the present study, no research had been conducted on the potential for indirect photolysis. In the case of indirect photolysis, target compounds react with photochemically-produced reactive intermediates (such as hydroxyl radicals). Additional background and discussion of results may be found in the research publication included as Appendix G (Plumlee et al., 2008c).

To explore the possibility of indirect photolysis of PFCs, selected perfluoroalkanesulfonamides were irradiated in aqueous hydrogen peroxide solutions using artificial sunlight to simulate aquatic environmental conditions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE), *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA), *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA), and perfluorooctane sulfonamide acetate (FOSAA). A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, perfluorooctane sulfonamide (FOSA), and perfluorooctanoate (PFOA) was developed (see Appendix F) and includes oxidation and *N*-dealkylation steps. As they did not undergo additional degradation, FOSA and PFOA were the final degradation products of hydroxyl radical-mediated indirect photolysis. UV-visible absorption spectra for the perfluorochemicals, showing absorbance in the UV region below the range of natural sunlight, are also reported.

Given the slow rates expected for biodegradation and limited sorption of PFCs, indirect photolysis of PFCs may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote Creeks study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending upon the sunlight and reactive intermediates available to facilitate indirect photolysis of PFCs.

3.5 PFC removal by membranes in advanced wastewater treatment

One of the project objectives was to make recommendations about potential treatment options for compounds that might interfere with the use of reclaimed water for stream augmentation. Concurrent to the laboratory and field investigations of the stream flow augmentation project, a supporting laboratory study on the rejection of PFCs by nanofiltration membranes was conducted. Rejections greater than 95% were measured for most compounds, and depended upon the solution pH (which controls the protonation state of the PFC) and the fouling layer. Details of the experimental approach and results may be found in the research publication included as Appendix H (Steinle-Darling and Reinhard, 2008). Additional data is contained in the Ph.D. thesis of Eva Steinle-Darling.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The major conclusions of the water quality monitoring campaign and supporting laboratory investigations are presented here, followed by project recommendations.

Analysis of NDMA by SPE-LC-MS/MS

1 The analytical method developed for NDMA in support of this project (Appendix C) features a high extraction efficiency using SPE and accurate identification and quantification via LC-MS/MS at a reporting limit of 2 ng/l, below the 10 ng/l notification level specified by the California Department of Health Services, and may be applied for additional nitrosamine analyses.

Water quality comparison of recycled water and site (surface and groundwater)

1 The assessment of the microconstituent risk associated with augmenting an urban stream with recycled wastewater is complicated by the fact that different constituents may be present in different concentrations in each water. In this project, the water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as NDMA and APEMs.

2 Some constituents were present in both waters (such as PFCs, organophosphates, and NBBS) at similar or different concentrations. The concentrations in the wastewater or at the site are likely to vary with time, and thus a more detailed evaluation of microconstituent concentration over time scales of days to months may be required to fully assess the impact of stream flow augmentation with recycled wastewater.

Perfluorochemicals in Water Reuse

1 As expected from their occurrence in wastewater and persistence during wastewater treatment, PFCs were detected in reclaimed wastewater from four California wastewater treatment plants that employ tertiary treatment (including the recycled water from the San Jose/Santa Clara Water Pollution Control Plant intended for the stream augmentation) and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat. A range of 90-470 ng/L total PFCs were detected in reclaimed wastewater, typically dominated by PFOA and PFOS. Concentrations of total PFCs in the water intended for the stream flow augmentation ranged 350-587 ng/l. Concentrations of PFOA and PFOS ranged 83-180 and 190-374 ng/l, respectively.

2 While many PFC monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other PFCs in the monitoring program may identify several additional PFCs resulting in a much greater total PFC concentration.

3 Though there was no known wastewater discharge into Upper Silver and Coyote Creeks, PFCs were found in the surface water and underlying groundwater at concentrations that were similar to the wastewater, highlighting the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement.

4 With respect to ecotoxicological effects, PFC release via recycled water into sensitive ecosystems requires evaluation (see Appendix E for further details). PFCs bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal dose which may be more ecotoxicologically relevant than the aquatic PFC concentration. One of five reclaimed wastewaters (the water intended for the augmentation in the present study) and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is protective of trophic level IV avian species that consume organisms in equilibrium with the water.

Attenuation of NDMA and Other Nitrosamines in Surface Water

1 Results show that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. Biotransformation of NDMA is not likely to be a significant process during river and groundwater transport in the Upper Silver Creek and Coyote Creek system.

2 NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight.

3 Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines.

4 Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively.

5 Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2}$ = 8-38 h at 244-855 W/m^2, 51° N latitude, 1 m depth).

Biotransformation of APEMs in Creek Sediment

1 Based on this study, significant biotransformation of APEMs could be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater.

2 However, literature research suggests that under aerobic conditions, relatively stable APECs may be formed. Under anaerobic conditions, biodegradation may

continue to form alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur.

3 Water quality monitoring of the surface and groundwater following stream flow augmentation with recycled water would be required to fully assess whether concentrations of APEMs, if detected, were significant following the expected attenuation and dilution with site water.

Hydroxyl-Radical Mediated Indirect Photolysis of Perfluoroalkanesulfonamides

1 In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA.

2 Final degradation products of the indirect photolysis of the perfluorooctanesulfonamides were PFOA and FOSA, which did not undergo additional degradation.

3 A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed and includes oxidation and *N*-dealkylation steps.

4 Given the slow rates expected for biodegradation and limited sorption, indirect photolysis of PFCs may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote Creeks study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending upon the sunlight and reactive intermediates available to facilitate indirect photolysis of PFCs.

Removal of PFCs by Nanofiltration

1 Rejections greater than 95% were measured for most PFCs tested (Appendix H), and depended upon the solution pH (which controls the protonation state of the PFC) and the fouling layer.

2 If nanofiltration or reverse osmosis were viable treatment options for wastewater prior to use in stream flow augmentation, these advanced treatment processes would result in adequate removal of PFCs.

Removal of NDMA by Reverse Osmosis

1 As suggested by results obtained in a separate study for an advanced wastewater treatment facility at the time of this project (Appendix C), microfiltration (MF) of wastewater effluent is not expected to reduce NDMA concentrations and may in fact lead to NDMA formation when in combination with chlorination or chloramination used to prevent MF membrane fouling.

2 Reverse osmosis (RO) treatment of secondary effluent using thin-film composite membranes typically results in NDMA rejection of approximately 50 to 65% or less. For the overall treatment train, this rejection is an important contribution to NDMA removal. Lower rejection may be associated with changing feed conditions and fouling observed in real treatment systems.

3 UV irradiation in combination with RO treatment and in some cases, blending, allows operators to reliably maintain the residual NDMA below the 10 ng/L CA drinking water notification level.

4 If RO was a viable treatment option for wastewater prior to use in stream flow augmentation, this advanced treatment process would likely result in a significant, through incomplete, removal of NDMA.

Based on the above conclusions, we can make the following broad recommendations:

1 A study with similar objectives should be executed at a site where ecological risks associated with reclaimed water release are minimized.

2 Applicable toxicological information is needed to interpret water quality data. Only one PFC toxicological modeling study (Rostkowski et al., 2006) was available, and its use led to the significant outcome of project cancellation.

3 Source control appears to be the only feasible way to reduce the release of PFCs into the environment. Thus, steps should be taken to minimize the use of PFCs that find their way into the environment.

5.0 REFERENCES

Anderson, M.P., 2005. Heat as a Ground Water Tracer. Ground Water 43, 951-968.

Buerge, I.J., Poiger, T., Mueller, M.D., Buser, H.R., 2003. Caffeine, an Anthropogenic Marker for Wastewater Contamination of Surface Waters. Environ. Sci. Technol. 37, 691-700.

Duffield, P., Bourne, D., Tan, K., Garruto, R., Duncan, M., 1994. Analysis of the neurotoxic plasticizer n-butylbenzenesulfonamide by gas chromatography combined with accurate mass selected ion monitoring. Journal of Analytical Toxicology 18, 361-368.

Green, S.A., Blough, N.V., 1994. Optical Absorption and Fluorescence Properties of Chromophoric Dissolved Organic Matter in Natural Waters. Limnology and Oceanography 39, 1903-1916.

Gross, B., Montgomery-Brown, J., Naumann, A., Reinhard, M., 2004. Occurrence and fate of pharmaceuticals and alkylphenol ethoxylate metabolites in an effluent-dominated river and wetland. Environ. Toxicol. Chem. 23, 2074-2083.

Gunnison, D., Zappi, M.E., Teeter, C., Pennington, J.C., Bajpai, R., 2000. Attenuation mechanisms of N-nitrosodimethylamine at an operating intercept and treat groundwater remediation system. Journal of Hazardous Materials 73, 179-197.

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. Environ. Sci. Technol. 39, 3946-3956.

Hoehn, E., Cirpka, O.A., 2006. Assessing hyporheic zone dynamics in two alluvial flood plains of the Southern Alps using water temperature and tracers. Hydrol. Earth Syst. Sci. 10, 553-563.

Jones & Stokes, 2000. Initial Study/Mitigated Negative Declaration, Coyote Creek Streamflow Augmentation Pilot Project. Prepared for City of San José Environmental Services Department.

Jonkers, N., Knepper, T.P., Voogt, P.D., 2001. Aerobic biodegradation studies of nonylphenol ethoxylates in river water using liquid chromatography-electrospray tandem mass spectrometry. Environ. Sci. Technol. 35, 335-340.

Lin, A.Y.-C., Plumlee, M.H., Reinhard, M., 2006. Natural attenuation of pharmaceuticals and alkylphenol polyethoxylate metabolites during river transport: photochemical and biological transformation. Environ. Toxicol. Chem. 25, 1458–1464.

Mallik, M.A.B., Tesfai, K., 1981. Transformation of Nitrosamines in Soil and in Vitro by Soil Microorganisms. Bulletin of Environmental Contamination and Toxicology 27, 115-121.

Montgomery-Brown, J., Li, Y., Ding, W.-H., Mong, G.M., Campbell, J.A., Reinhard, M., 2008. NP1EC Degradation Pathways Under Oxic and Microxic Conditions. Environ. Sci. Technol. DOI: 10.1021/es702561t.

Montgomery-Brown, J., Reinhard, M., 2003. Occurrence and Behavior of Alkylphenol Polyethoxylates in the Environment. Environmental Engineering Science 20, 471-486.

Pehlivanoglu-Mantas, E., Sedlak, D.L., 2006. The fate of wastewater-derived NDMA precursors in the aquatic environment. Water Res. 40, 1287-1293.

Plumlee, M.H., Larabee, J., Reinhard, M., 2008a. Perfluorochemicals in Water Reuse. Chemosphere 72, 1541-1547.

Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P., Reinhard, M., 2008b. *N*-Nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV Treatment and Analysis via LC-MS/MS. Water Res 42, 347-355.

Plumlee, M.H., McNeill, K., Reinhard, M., 2008c. Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides, in progress.

Plumlee, M.H., Reinhard, M., 2007. Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water. Environ. Sci. Technol. 41, 6170-6176.

Reinhard, M., Ding, J., 2001. Organic Contaminant Behavior During Wetland Treatment and Groundwater Recharge. SARWQH 1998-2000. Orange County Water District, Fountain Valley, CA.

Reinhard, M., Ding, W.-H., Zhou, J., Orwin, E., 1999. Organic Contaminant Behavior During Groundwater Recharge with Reclaimed Wastewater and Santa Ana River Water: A Laboratory and Field Evaluation. Department of Civil Engineering, Stanford University, Stanford, CA 94305-4020.

Rostkowski, P., Yamashita, N., So, I.M.K., Taniyasu, S., Lam, P.K.S., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K., Giesy, J.P., 2006. Perfluorinated Compounds in Streams of the Shihwa Industrial Zone and Lake Shihwa, South Korea. Environ. Toxicol. Chem. 25, 2374-2380.

SCVWD, 2004. Workplan: Impact Evaluation of Stream Flow Augmentation with Tertiary Recycled Water in Coyote Creek. Submitted to The Metropolitan Water District of Southern California, Agreement No. 41808, by Santa Clara Valley Water District.

SCVWD, 2007. Initial Study/Mitigated Negative Declaration: Stream Flow Augmentation Project Silver Creek/Coyote Creek Initial Study.

Sharp, J.O., Wood, T.K., Alvarez-Cohen, L., 2005. Aerobic biodegradation of N-nitrosodimethylamine (NDMA) by axenic bacterial strains. Biotechnology and Bioengineering 89, 608-618.

Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292-5297.

Tate, R.L., Alexander, M., 1976. Resistance of nitrosamines to microbial attack. Journal of Environmental Quality 5, 131–133.

Yang, W.C., Gan, J., Liu, W.P., Green, R., 2005. Degradation of N-Nitrosodimethylamine (NDMA) in Landscape Soils. Journal of Environmental Quality 34, 336-341.

GLOSSARY

APEMs	metabolites of alkylphenol ethoxylates
MF	microfiltration
NBBS	*N*-butylbenzene sulfonamide
NDMA	*N*-nitrosodimethylamine
PFCs	perfluorochemicals
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
RO	reverse osmosis
SCVWD	Santa Clara Valley Water District

APPENDICES

Appendix A	Water quality data table for constituents monitored by SCVWD
Appendix B	"Upper Silver Creek Experimental Site Exploration and Characterization" by Eduard Hoehn, 2006. Project report for Eawag, Swiss Federal Institute of Water Science and Technology.
Appendix C	Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P., Reinhard, M., 2008. *N*-Nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV Treatment and Analysis via LC-MS/MS. Water Res 42, 347-355.
Appendix D	Plumlee, M.H., Reinhard, M., 2007. Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water. Environ. Sci. Technol. 41, 6170-6176.
Appendix E	Plumlee, M.H., Larabee, J., Reinhard, M., 2008. Perfluorochemicals in Water Reuse. Chemosphere 72, 1541-1547.
Appendix F	Montgomery-Brown, J., Li, Y., Ding, W.-H., Mong, G.M., Campbell, J.A., Reinhard, M., 2008. NP1EC Degradation Pathways Under Oxic and Microxic Conditions. Environ. Sci. Technol. DOI: 10.1021/es702561t.
Appendix G	Plumlee, M.H., McNeill, K., Reinhard, M., 2008. Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides, in progress.
Appendix H	Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292-5297.